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REGISTERED NO. M. 3121

PROCEEDINGS

OF THE

INDIAN ACADEMY

OF SCIENCES

VOL. IX] *SECTION A* [NO. 1

JANUARY, 1939

Price Rs. 2 or 3 Sh. *Annual Subscription Rs. 18*

PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY G. SRINIVASA RAO,
SUPERINTENDENT, AND PUBLISHED BY THE INDIAN ACADEMY OF SCIENCES,
HEBBAL, BANGALORE.

Cpt
Indian academy
10-8-43
4760 d
v. 9, no. 1-6

FIXATION OF THE AROMATIC DOUBLE BONDS IN THE CHROMONES

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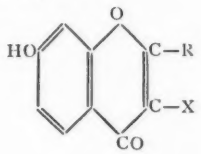
Received October 19, 1938

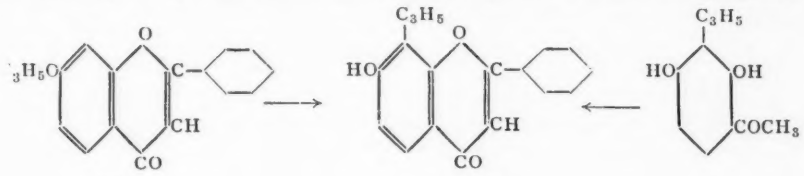
In the course of work in progress in these laboratories relating to the preparation of aldehydes from 7-hydroxy-chromones it has been found that the incoming aldehyde group occupies position 8 indicating thereby that it is the reactive position. Wittig *et. al.*[1] and later on Baker[2] showed that when 7-acetoxy-chromones are subjected to Fries migration the acetyl group wanders only to the eighth position. These results suggested therefore the possibility of the aromatic double bonds in chromones occupying the positions as shown in (I).



where R is CH_3 or C_6H_5
and X is H or OCH_3

(I)

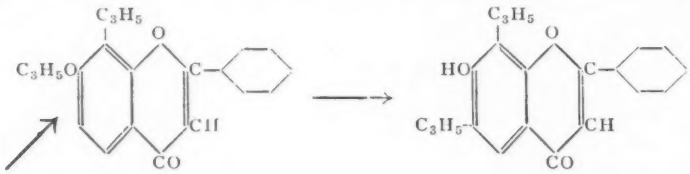
With a view to bring forward further definite evidence regarding (1) the distribution of the aromatic double bonds in the chromones and (2) the extent to which this distribution is alterable when made necessary, experiments conducted with 7-hydroxy-flavone and 2-methyl-3-methoxy-7-hydroxy-chromone are recorded in this paper. Since Claisen transformation of the allyl ethers offers the most reliable information regarding the position of the double bonds this reaction has been studied in detail. 7-Allyloxyflavone (II) underwent smooth and almost quantitative transformation into 8-allyl-7-hydroxyflavone (III). The constitution of the transformation product was established by its synthesis from 3-allylresacetophenone which was prepared



(II) (III)

according to the method of Baker and Lothian.[3] This gives therefore definite proof that position 8 is the reactive one in 7-hydroxyflavone and that the bond distribution is as represented in formula (I).

To find out how far this distribution is rigid the eighth position was next blocked by means of a protecting group (allyl) and the behaviour of 8-allyl-7-hydroxyflavone examined. The allyl ether of this (IV) underwent again Claisen transformation to give a good yield (75 per cent.) of an isomeric hydroxycompound which is obviously 6 : 8-diallyl-7-hydroxyflavone (V). The allyl ether has evidently reacted in the form (IV) rendering the sixth position active. The reactivity of the sixth position in compounds with substituents in position 8 was also exhibited when they were coupled in alkaline solution with diazotised *p*-nitraniline. 8-allyl-7-hydroxyflavone (III), 8-methyl-7-hydroxyflavone (VI) and 8-methyl-7-hydroxy-3-methoxyflavone[4] yielded highly coloured dyes under the above conditions. This is explicable only if structures similar to (IV) are assumed for these compounds.



(IV) (V)

Results of a similar nature were obtained from 2-methyl-3-methoxy-7-hydroxychromone. Its allyl ether (VII) underwent smooth conversion into 2-methyl-3-methoxy-7-hydroxy-8-allylchromone (VIII). The constitution of (VIII) was obtained from analogy with the compound of the 7-hydroxyflavone series. The important point to be noted however is that the allyl ether (IX) of this compound in turn underwent Claisen transformation to give an isomeric phenolic compound which is evidently 2-methyl-3-methoxy-6 : 8-diallyl-7-hydroxychromone (X). The 8-allyl-7-hydroxy chromone (VIII) further gave rise to a coloured azodye on being coupled with diazotised *p*-nitraniline. It is therefore concluded that while chromones generally react in form (I), reactivity in the isomeric form (IV) is not precluded.

Experimental

7-Allyloxyflavone (II).—A solution of 7-hydroxyflavone (2 g.) in anhydrous acetone (40 c.c.) was treated with allylbromide (5 c.c.) and anhydrous potassium carbonate (5 g.) and boiled under reflux for about six hours. The solvent was then distilled off and dilute hydrochloric acid added to the residue. An oily product was thereby obtained. It was extracted

with ether and the ether solution shaken with dilute alkali so as to remove any unchanged hydroxyflavone. On removing the solvent a pale yellow crystalline solid was left behind. This was easily recrystallised from a mixture of benzene and petroleum ether (1 : 4) and thus the allyloxy compound was obtained in the form of colourless rhombic plates and rectangular prisms melting at 95–96°. The yield of the pure substance was one gram. (Found : C, 77·7 ; H, 5·1 ; $C_{18}H_{14}O_3$ requires C, 77·7 ; H, 5·0 per cent.)

8-*Allyl-7-hydroxyflavone* (*III*).—The above allyl ether (0·2 g.) was heated in an oil-bath at 210–15° for 2½ hours. The substance rapidly melted and the molten liquid slowly underwent conversion into a crystalline solid. After two crystallisations from alcohol it was obtained as colourless flat needles melting at 245–46°. It gave no colour with ferric chloride in alcoholic solution. (Found : C, 73·2 ; H, 5·7 ; $C_{18}H_{14}O_3$, H_2O requires C, 73·0 ; H, 5·4 per cent.) The yield of the final product was 0·12 g. and the sample was found to be identical in all respects with the one synthesised from 3-allylresacetophenone as described below :

3-Allylresacetophenone was prepared in very good yield by the method of Baker and Lothian.[3] The ketone (2·5 g.) was heated with sodium benzoate (5 g.) and benzoic anhydride (12 g.) for five hours under reduced pressure in an oil-bath at 190°. The product containing the benzoyloxyflavone was debenzoylated by boiling for half an hour with 100 c.c. of 10 per cent. alcoholic potash. The alcohol was then distilled off, water added and the resulting solution saturated with carbon dioxide. 8-Allyl-7-hydroxyflavone was precipitated as a crystalline solid. When recrystallised from alcohol it was obtained as flat needles melting at 245–46°. (Found : C, 73·0 ; H, 5·0 ; $C_{18}H_{14}O_3$, H_2O requires C, 73·0 ; H, 5·4 per cent.) Yield was one gram. A mixture of it with the sample obtained by the Claisen transformation had the same melting point.

7-*Allyloxy*-8-*allylflavone* (*IV*)—was prepared by heating the above 7-hydroxy-8-allylflavone in acetone solution with allylbromide and anhydrous potassium carbonate. On removing the solvent and adding water, a crystalline solid was produced which on further crystallisation from alcohol yielded the allyloxy compound as sheaves of thin needles melting at 145–46°. (Found : C, 79·0 ; H, 5·7 ; $C_{21}H_{18}O_3$ requires C, 79·3 ; H, 5·7 per cent.) The yield was 0·9 g. from 1 g. of the hydroxyallylflavone.

6 : 8-*Diallyl-7-hydroxyflavone* (*V*).—The above allyl ether (0·4 g.) was heated for 2½ hours at 210–15°. The molten mass did not show any sign of crystallisation even after cooling. On boiling it with alcohol a small amorphous portion remained insoluble. The alcoholic solution was turbid ;

the addition of a drop of aqueous calcium chloride precipitated a small quantity of a deeply coloured high melting solid. Though the solution was now clear, it was coloured and contained some resinous matter which was precipitated by the gradual addition of water. The resin separated out first and was removed. The main product was deposited subsequently. By repeating this process of solution in alcohol and fractional precipitation with water a product melting between 180°–90° was obtained in 75 per cent. yield. Further crystallisation from alcohol and from glacial acetic acid yielded 6 : 8-diallyl-7-hydroxyflavone in the form of thin rectangular plates melting at 196–98°. The compound gave no colour with ferric chloride and was sparingly soluble in cold alkali though solution was effected by warming. On cooling the warm alkaline solution the sparingly soluble potassium salt separated as a pale yellow cotton-wool like mass. (Found : C, 78·9 ; H, 5·8 ; $C_{21}H_{18}O_3$ requires C, 79·3 ; H, 5·7 per cent.)

2-*Methyl*-3-*methoxy*-7-*allyloxychromone* (*VII*)—was obtained in an almost quantitative yield by heating 2-methyl-3-methoxy-7-hydroxychromone[5] in acetone solution with allylbromide and potassium carbonate. After removing the solvent and adding water, the solid product was macerated with cold dilute alkali in order to remove the unchanged hydroxychromone. The allyl ether was easily soluble in alcohol and crystallised out as narrow rectangular plates melting at 94–95°. (Found : C, 67·8 ; H, 6·0 ; $C_{14}H_{14}O_4$ requires C, 68·3 ; H, 5·7 per cent.)

2-*Methyl*-3-*methoxy*-7-*hydroxy*-8-*allylchromone* (*VIII*).—The transformation of the above allyl ether (VII) was effected best by heating it for 2½ hours at 200° as uniformly as possible. The product (8-allyl-7-hydroxy compound) was obtained readily pure in almost quantitative yield. It crystallised from alcohol as colourless rectangular rods melting at 183–84°. (Found : C, 64·0 ; H, 5·9 ; $C_{14}H_{14}O_4$, H_2O requires C, 63·6 ; H, 6·1 per cent.) If a higher temperature (205–15°) was employed considerable resinification took place and the transformation product had to be purified with great difficulty, whereas at a lower temperature (180–200°) the change was only partial and the resulting mixture had to be separated by using aqueous potash. The alkali-soluble portion on recrystallisation from alcohol gave the desired product, whereas the insoluble portion was the unchanged allyl ether.

2-*Methyl*-3-*methoxy*-7-*allyloxy*-8-*allylchromone* (*IX*).—The above 7-hydroxy-8-allylchromone (VIII) was converted into the allyl ether by the procedure already described. The oily product solidified to an amorphous solid when left in the ice-chest for several hours. It was macerated with cold dilute alkali in order to remove the unchanged hydroxycompound and then extracted with small quantities of petroleum ether. A small highly

coloured portion remained undissolved. By slow evaporation of the combined petroleum ether solution the required allyl ether was obtained in a colourless, crystalline form and in 90 per cent. yield. A repetition of the crystallisation from the same solvent yielded the product as rectangular rods melting at 66–68°. (Found: C, 71·2; H, 6·6; $C_{17}H_{18}O_4$ requires C, 71·3 H, 6·3 per cent.)

2-*Methyl*-3-*methoxy*-6 : 8-*diallyl*-7-*hydroxychromone* (*X*).—The preparation of this compound from the above ether (IX) was rather tedious and the yield consequently poor. The Claisen transformation was effected at 200°–05°. The viscous semi-solid product underwent partial solution when macerated for a long time with dilute sodium hydroxide. The brown solution was filtered and acidified. The colourless solid thereby precipitated was contaminated with some resinous matter. It was twice crystallised from alcohol. The first crops of crystals were contaminated with resin and were discarded. A final crystallisation from dilute acetic acid yielded the diallyl-7-hydroxychromone as thin rectangular plates melting at 120–21°. (Found: C, 69·3; H, 6·7; $C_{17}H_{18}O_4$, $\frac{1}{2}$ H_2O requires C, 69·2; H, 6·4 per cent.) The substance dissolved slowly in dilute sodium hydroxide and gave a pale brown colour with ferric chloride.

7-*Hydroxy*-8-*methylflavone* (*VI*).—An intimate mixture of 3-methyl resacetophenone[4] (0·5 g.), sodium benzoate (1 g.) and benzoic anhydride (3 g.) was heated under reduced pressure for 4 hours in an oil-bath at 190°. The product was then refluxed for half an hour with 10 per cent. alcoholic potash (20 c.c.) in order to effect the hydrolysis of the benzoyloxy group. After removal of the solvent the residue was dissolved in water (30 c.c.) and the clear solution saturated with carbon dioxide. The precipitated hydroxy methylflavone was crystallised from alcohol (charcoal) whereby it was obtained in the form of short colourless rectangular prisms melting at 255–57°. The alcoholic solution did not give any characteristic colour with ferric chloride. (Found: C, 70·8; H, 5·4; $C_{16}H_{12}O_3$, H_2O requires C, 71·1; H, 5·2 per cent.)

Summary

7-Allyloxyflavone undergoes Claisen transformation to form 8-allyl-7-hydroxyflavone, the constitution of which is established from its synthesis from 3-allyl-resacetophenone. The bond distribution should therefore be as in (I). However 8-alkyl substituted derivatives undergo coupling with diazotised *p*-nitraniline to form dyes and 7-allyloxy-8-allylflavone undergoes further transformation to form 6 : 8-diallyl-7-hydroxy-flavone. Closely analogous results are obtained from 2-methyl-3-methoxy-7-hydroxy-chromone. It is therefore concluded that though the chromones generally

react in form (I) the alternative disposition of the bonds (IV) is not precluded.

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7-HYDROXYCHROMONE-8-ALDEHYDES AND THEIR CONVERSION INTO CHROMONO-7:8-α-PYRONES

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Received November 5, 1938

The preparation of aldehydes starting from 7-hydroxy-3-methoxyflavone, 7-hydroxy-2-methyl-3-methoxychromone and 7-hydroxy-flavone is described in this paper. The hydroxy compounds undergo condensation with hexamethylene-tetramine in glacial acetic acid solution easily and on subsequent hydrolysis with hydrochloric acid give comparatively good yields of the aldehydes.[1] That the aldehyde group enters the eighth position has been established by reducing the compound derived from 7-hydroxy-3-methoxyflavone using palladium-charcoal and hydrogen. The resulting methyl substituted flavone is found to be identical with 3-methoxy-7-hydroxy-8-methylflavone whose preparation starting from 2-methylresorcinol has already been described.[2] The reactive position in 7-hydroxy-chromones is therefore the eighth one just as in the case of the 7-hydroxycoumarins.

The hydroxychromones do not undergo condensation with malic acid in the presence of sulphuric acid. The hydroxychromone-aldehydes however react easily with sodium acetate and acetic anhydride (Perkin's reaction) to yield chromono-7 : 8-α-pyrones.

Experimental

7-Hydroxy-3-methoxyflavone-8-aldehyde.–7-Hydroxy-3-methoxyflavone was obtained from ω-methoxyresacetophenone by the method of Allan and Robinson.[3] 2 g. of this flavone were heated with hexamethylenetetramine (6 g.) and glacial acetic acid (20 c.c.) for 6 hours in a boiling water-bath. The clear hot solution was then treated with a boiling mixture of fuming hydrochloric acid (10 c.c.) and water (20 c.c.). It rapidly became turbid and began to deposit needle-shaped crystals of the aldehyde in a few minutes. By leaving overnight, a very good yield of the solid was obtained and this was fairly pure. After filtering and washing with water one crystallisation from glacial acetic acid rendered it quite pure. It melted at 222–23°, the yield being 1·3 g. (Found : C, 68·4 ; H, 4·0 ; $C_{17}H_{12}O_5$ requires C, 68·9, H 4·1%.)

The compound was rather sparingly soluble in alcohol, more easily in glacial acetic acid and readily in pyridine. From acetic acid it came down as shining yellow crystals which appeared as rectangular plates under the

microscope. It was insoluble in cold dilute alkali and only slightly soluble on heating. With alcoholic ferric chloride it gave a brown pink colour. The phenylhydrazone crystallised from alcohol as yellow rectangular rods decomposing at 149–51°. (Found : N, 7·2, loss on drying (at 105°) 4·5 ; $C_{23}H_{18}O_4N_2$, I H_2O requires N, 6·9, loss on drying 4·5%.)

Reduction to 3-methoxy-7-hydroxy-8-methylflavone.—The aldehyde (0·5 g.) was dissolved in glacial acetic acid (120 c.c.), palladium-charcoal (2 g.) added and the mixture shaken in an atmosphere of hydrogen till two molecular proportions of the gas were absorbed. The solution was then filtered and the solvent removed by distillation under reduced pressure. When the residue was crystallised thrice from alcohol colourless rectangular plates of the reduction product were obtained. (Found: C, 71·7 ; H, 5·2 ; $C_{17}H_{14}O_4$ requires C, 72·3, H, 5·0%.) The substance melted at 255–56° and a mixture of it with the sample prepared from 2-methylresorcinol[2] melted at the same temperature.

3-Methoxyflavono-7 : 8-α-pyrone.—The above hydroxyaldehyde (0·3 g.) was heated with anhydrous sodium acetate (1 g.) and acetic anhydride (10 c.c.) for 6 hours in an oil-bath maintained at 175–85°. The mixture was then poured into excess of cold water (30 c.c.) and left overnight. The solid that separated was filtered and crystallised twice from acetic acid. The flavono-α-pyrone was thus obtained as colourless flat needles melting at 254–55°. (Found: C, 70·8 ; H, 4·0 ; $C_{19}H_{12}O_5$ requires C, 71·3 ; H, 3·8%.) The compound was sparingly soluble in alcohol and easily in acetic acid and it gave no colouration with alcoholic ferric chloride. It was almost insoluble in cold dilute alkali, but dissolved rapidly on heating to produce a clear deep yellow solution.

2-Methyl-3-methoxy-7-hydroxychromone.—The 7-acetoxycompound (m.p. 113°) was obtained from ω-methoxyresacetophenone by the method of Allan and Robinson.[3] The subsequent hydrolysis has now been effected more quickly and conveniently by heating with 5 per cent. aqueous potash until complete solution is just effected (3–5 minutes), cooling immediately and acidifying the solution. The hydroxychromone crystallised from alcohol as long thin prismatic needles melting at 214–15°.

2-Methyl-3-methoxy-7-hydroxychromone-8-aldehyde.—This was obtained by essentially the same method as was adopted in the case of the methoxyflavone-aldehyde. After hydrolysis by means of boiling hydrochloric acid, the mixture had to be distilled under reduced pressure in order to remove most of the acetic and hydrochloric acids and then treated with water before the required aldehyde could be made to separate as a crystalline solid. When recrystallised from aqueous alcohol it came down as large rectangular prisms melting at 180–81°. (Found : C, 61·2 ; H, 4·7 ; $C_{12}H_{10}O_5$ requires C, 61·6 ;

H, 4·3%.) The yield of the pure aldehyde was 0·8 g. from 2 g. of the chromone. It gave a blood red colour with alcoholic ferric chloride. Its phenylhydrazone crystallised from alcohol as glistening hexagonal plates and melted at 220–22°. (Found : N, 9·0 ; $C_{18}H_{16}O_4N_2$ requires N, 8·7%.)

2-*Methyl*-3-*methoxychromono*-7 : 8-*α-pyrone*—was obtained from the above aldehyde by heating with sodium acetate and acetic anhydride. It was sparingly soluble in alcohol and fairly easily soluble in acetic acid from which it crystallised in the form of pale yellow needles which turned brown at about 250° and melted at 282–84°. (Found : C, 64·8 ; H, 4·1 ; $C_{14}H_{10}O_5$ requires C, 65·1; H, 3·9%.) The substance was unaffected by cold dilute alkali but dissolved on heating to give an orange coloured solution.

7-*Hydroxyflavone*-8-*aldehyde*.—7-Hydroxyflavone (Robinson and Venkataraman[4]) was condensed with hexamethylenetetramine and the product hydrolysed with boiling hydrochloric acid as described before. The aldehyde slowly separated out as a pale yellow crystalline solid. It was moderately soluble in alcohol and it dissolved easily in hot acetic acid and pyridine. From acetic acid it separated out in the form of large crystals while from alcohol it came out as clusters of fine needles and narrow plates which melted at 223–24°. With alcoholic ferric chloride it gave an orange red colour and it was only slowly dissolved by dilute alkali. (Found : C, 71·7 ; H, 3·7 ; $C_{16}H_{10}O_4$ requires C, 72·2; H, 3·8%.) The yield of the pure aldehyde was 0·8 g. from 2 g. of the flavone.

Flavono-7 : 8-*α-pyrone*—was obtained from the above aldehyde by the action of sodium acetate and acetic anhydride. It crystallised from hot glacial acetic acid as colourless fine needles and narrow plates melting at 250°. (Found : C, 74·6 ; H, 3·9 ; $C_{18}H_{10}O_4$ requires C, 74·5 ; H, 3·5%.) In its solubility in alcohol and pyridine and in its reaction towards aqueous alkali it resembled the other α-pyrones described previously.

Summary

Starting from 3-methoxy-7-hydroxyflavone, 2-methyl-3-methoxy-7-hydroxychromone and 7-hydroxyflavone aldehydes have been prepared. In these compounds the aldehyde groups occupy the eighth positions. By the action of sodium acetate and acetic anhyrdide the corresponding chromono- and flavono-α-pyrones have been synthesised.

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THE BEHAVIOUR OF ORGANIC SOLIDS ON THE SURFACE OF WATER

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Received October 21, 1938

The peculiar behaviour of camphor on the surface of water is a classical example of a general phenomenon characteristic of many solid organic compounds. A number of other substances have been more recently found to exhibit a similar behaviour (*vide* Geppert[1], Edwards[2] and Ramdas[3]). The factors determining these movements on the surface of water seem to be rather complex. Undoubtedly the non-uniform lowering of the surface tension is the major factor. For the vigour and persistence of the movements the substance which spreads as a film must be capable of subsequent diffusion inside the bulk of the liquid by solution or of leaving the surface by vaporisation. Since the lowering of the surface tension and the solubility of a substance with reference to a particular solvent are dependent largely upon its chemical nature, a large number of chemical compounds belonging to different groups have now been examined with respect to their behaviour on the surface of water.

In order that the observations may be correct it is very necessary that the utmost cleanliness be observed. The vessels used, cylindrical glass troughs 6″ in diameter, were submitted to treatment with hot chromic acid followed by thorough washing with running tap-water. Wherever the purity of the samples was doubted they were recrystallized from suitable solvents, dried and the pure dry samples employed for the investigation. Touch of the fingers was scrupulously avoided as it was usually sufficient to impair, if not arrest, the movements in many cases by communicating a film of grease to the water surface. The substance was generally added with a spatula (freed from grease) from the least possible distance so as to minimise any mechanical disturbances and the water surface was as far as possible protected from air draughts. From the results of observation substances have been classified into three gourps : A, B and C. Those that show vigorous movements are placed under A, those that show slow movements under B and the indifferent ones under C.

A	B	C
	ACIDS	
1 Acetyl-salicylic	1 *m*-Amino benzoic	1 *p*-Amino benzoic
2 *o*-Amino benzoic	2 Diphenic	2 Gallic
3 α-Amino butyric	3 Fumaric	3 Naphthionic
4 Amygdalic	4 Hippuric	4 Palmitic
5 Benzoic	5 Proto-catechuic	5 Stearic
6 Cinnamic		6 Sulphanilic
7 Citraconic		
8 Glutaric		
9 Maleic		
10 Malic		
11 Malonic		
12 Mesaconic		
13 β-Naphthalenesulphonic		
14 *o*-Nitrobenzoic		
15 Phenyl acetic		
16 Phthalic		
17 Salicyclic		
18 Succinic		
	ANHYDRIDES	
1 Succinic	nil	nil
2 Phthalic		
	CARBONYL COMPOUNDS	
1 Antipyrin	nil	1 Anthraquinone
2 Benzophenone		2 Michler's ketone
3 Camphor		3 *p*-Nitrobenzaldehyde
4 Coumarin		
4 Dimethyl-γ-pyrone		
6 Menthone		
7 *o*-Nitrobenzaldehyde		
8 Quinone		
9 Vanillin		

A	B	C
	AMIDES AND AMINO COMPOUNDS	
1 Acetamide	1 Benzanilide	1 6-Aminocoumarin
2 *o*-Acetotoluide	2 Diphenylamine	2 Benzidine
3 Benzamide	3 *p*-Phenylenediamine	3 Carbazole
4 Benzenesulphonamide	4 Phthalimide	4 Diphenylurea
5 Chloracetamide	5 *m*-Nitraniline	5 Hydrazobenzene
6 α-Naphthylamine		6 Malonamide
7 *o*-Nitroaniline		7 β-Naphthylamine
8 *m*-Phenylenediamine		8 *p*-Nitroaniline
9 *o*-Phenylenediamine		9 Oxamide
10 Phenylsemicarbazide		10 Oxanilide
11 Propionamide		11 Succinamide
12 Salicylamide		
	HYDROXY COMPOUNDS	
1 Borneol	1 7-Hydroxy-4-methyl coumarin	1 Nitroso-β-naphthol
2 Hydroquinone		2 Phenolphthalein
3 α-Naphthol		3 Quercetin
4 β-Naphthol		4 Tetrahydroxy-anthraquinone
5 *m*-Nitrophenol		
6 *o*-Nitrophenol		
7 *p* Nitrophenol		
8 Pyrocatechol		
9 Quinhydrone		
10 Resorcinol		
	ESTERS	
1 Glyceryltribenzoate	1 Phenyl benzoate	1 4-Methyl-umbeliferone acetate
	2 Phenyl salicylate	2 Acetyl-quercetin

A	B	C
	HYDRO-CARBONS	
Nil	Nil	1 Acenaphthene 2 Anthracene 3 Diphenyl 4 Naphthalene 5 Phenanthrene 6 Triphenyl-methane
	MISCELLANEOUS	
1 *p*-Nitroanisole 2 *p*-Nitro-toluene 3 Brucine	Nil	1 Azo-benzene 2 *m*-Dinitrobenzene 3 Dinitronaphthalenes (1 : 5 and 1 : 8) 4 *p*-Dibromobenzene 5 Hexachlorobenzene 6 α-Nitronaphthalene 7 Congo red.

The above list is neither complete nor comprehensive and various factors have limited the availability of suitable compounds. It is not possible therefore to venture any generalisation. But certain outstanding features may be noticed. There are certainly wide variations in the behaviour of substances. The hydrocarbons as a rule do not exhibit any movement. This seems to agree with the observations of Ramdas regarding the behaviour of liquid hydrocarbons. The introduction of a nitro group seems to have a varying influence. Nitrotoluene exhibits vigorous movement whereas *m*-dinitrobenzene, α-nitronaphthalene and dinitro-naphthalenes show no movement. Halogen substitution does not favour movement as can be seen from the behaviour of *p*-dibromobenzene and hexachlorobenzene.

The carboxylic acids and anhydrides in general exhibit vigorous movements. In regard to these the following points are noteworthy. Maleic acid comes under A and its isomer fumaric acid belongs to B. *o*-Amino-benzoic acid (A) differs from its isomerides *m*-amino-benzoic acid (B) and *p*-amino-benzoic acid (C). Only a few of the acids come under C. The presence of palmitic and stearic acids in this group may be easily understood

because they saturate the surface immediately. Obviously the influence of the COOH-groups, which in general favours rapid movement, can be completely controlled by other factors. As a rule carbonyl compounds come under A, none under B and a few under C. So the carbonyl group may be considered as one favouring quick movement. The amides and amino-compounds are represented in all the three categories. It is to be noted that here also the position of the groups affects considerably the behaviour of the substances. As examples the isomeric nitroanilines, naphthylamines and phenylenediamines may be mentioned. The simpler hydroxy compounds belonging to the group of phenols exhibit good movement whereas those having larger sizes and complex structures have very little movement. Esters in general do not exhibit vigorous movements. The introduction of an aliphatic residue favours the movements as in the case of glyceryltribenzoate.

	Name of the substance	Percent lowering of surface tension	Classification of the movement
1	Phenylacetic acid ..	32·46	A
2	Camphor ..	25·85	A
3	Dimethyl-γ-pyrone ..	21·23	A
4	Maleic acid ..	12·22	A
5	Benzoic acid ..	11·60	A
6	Coumarin ..	8·01	A
7	Succinic acid ..	7·94	A
8	Phthalic acid ..	4·72	A
9	*p*-Nitrotoluene ..	4·60	A
10	*o*-Nitrophenol ..	3·30	A
11	Phthalimide ..	2·40	B
12	Fumaric acid ..	1·30	B
13	Diphenylamine ..	0·92	B
14	Anthracene ..	< 0·3	C
15	Diphenyl ..	< 0·3	C
16	Hydrazobenzene ..	do.	C
17	Naphthalene ..	do.	C
18	Sulphanilic acid ..	do.	C

With a view to get an idea as to the relative extent of lowering of the surface tension of water produced by substances which exhibit the movements and also to correlate the behaviour of the substances with their effect on the surface tension we determined the surface tension of the solutions of a few typical compounds. In each case excess of the substance was shaken with water for fifteen minutes and the surface tension of the filtered solution determined by the capillary rise method at 27° C. The results of our findings are given in the above table.

The movements exhibited by phenyl-acetic acid are the most spectacular of all. They are by far more vigorous than those of camphor or *p*-toluidine or any other vigorously moving substance. Its position in the table above is quite consistent with its remarkably vigorous movements. Hydrocarbons and other inert substances belonging to the class C have very negligible effect on the surface tension of water, the percentage differences being within the limits of experimental error. Substances which lower the surface tension by 3 or 4 per cent. are capable of exhibiting vigorous movements. Maleic acid and fumaric acid exhibit considerable difference in their capacity to lower the surface tension of water and this easily explains their difference in behaviour on the surface of water. The lowering produced by benzoic acid is 11·6 per cent., but its movements are more vigorous than those of maleic acid though the latter lowers to the extent of 12·22 per cent. This is due to the fact that maleic acid is more soluble in bulk and as a particle of it moves some distance it gets dissolved and thus disappears. *o*-Nitrophenol and phthalimide exhibit far more differences in their movements than is indicated by the surface tension of their solutions. It is thus evident that while the lowering of the surface tension of water is a necessary condition for exhibiting the movements on its surface the vigour and persistence of the movements are controlled by several other factors. The chief among them may be density, solubility, rate of solution on the surface or in bulk, rate of evaporation, etc.

During the course of the above investigations we had occasion to observe combination movements exhibited by two pairs of substances. When small pieces of phenyl-acetic* acid are added one after another to a clean water surface a stage is reached when they all remain steady without showing any movement. When on this surface a small piece of camphor is placed so that it does not touch any particle of phenyl acetic acid it is found that the camphor particle also remains steady. If however the camphor particle is

* Saturation of the water surface first with Camphor and subsequent addition of Phenyl acetic acid gives rise to more spectacular Combination movements.

made to come into contact with a particle of phenyl acetic acid these two form a couple and begin to move about very vigorously till their combination ceases by colliding either with the walls of the vessel or with any other bigger floating particle, and then both come to a stop. A similar combination is observed with the substances *p*-nitrotoluene and *o*-nitrophenol. In both these cases droplets of liquid are found to be shot out in the direction opposite to that of the movement. We are inclined to feel that these combination movements may be caused by the recoil effects produced when droplets of the molten substance leave the solid. The melting is obviously caused by each substance lowering the melting point of the other.

Summary

A large number of organic compounds belonging to different groups have been studied in regard to their behaviour on the surface of water. The influences of the various groups — COOH, $> C = O$, $- NH_2$, etc. in a substance on its behaviour on the water surface are discussed.

Percentage lowering of surface tension of aqueous solutions of a number of typical compounds are recorded and the results compared with their behaviour on the water surface.

Combination movements exhibited by the pairs phenylacetic acid—camphor and *p*-nitrotoluene—*o*-nitrophenol are described.

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AN APPLICATION OF THE THEORY OF FINITE STRAIN

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Received October 28, 1938

The theory of finite strain in elastic problems has been developed on the hypothesis that the second order terms in the components of strain may not be neglected.[1] Like the body-stress equations these components have been referred to the actual position of a point P of the material in the strained condition, and not to the position of a point considered before strain. Many applications of this theory have been already worked out.[2] The object of the present paper is to apply it to the discussion of the vertical oscillations of a particle attached to an elastic string, the amplitude of oscillations having any value subject to the conditions that the limits of perfect elasticity are not surpassed and the string remains isotropic throughout. As is well known the period of oscillation in such cases is not necessarily independent of the amplitude of oscillation.

A mass m is attached to one end of a light elastic string whose other end is fixed. The unstretched length of the string is l, and the increase in its length in the position of equilibrium is L. Some writers use the initial stretched length for the unstretched length of the string in the Hooke's formula. This makes no difference when the stretch is small, but not when the string is sufficiently stretched. Again, the generalized Hooke's Law should not be now used. The tension and stretch are connected by means of the formula[3]

$$T = \tfrac{1}{2} E \left[1 - \frac{1}{(1+S)^2} \right], \tag{1}$$

where

$$S = \frac{\text{Increase in length}}{\text{unstretched length}},$$

and E is Young's modulus.

This relation reduces to $T = E S$ when S^2 and higher process of S can be neglected.

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[1] Seth, *Phil. Trans. Roy. Soc.*, 1935, **234**, (A), 231–64.

[2] Seth, *Loc. cit.*; Seth and Shepherd, *Proc. Roy. Soc.*, 1936, **156**, (A), 171–92.

[3] Seth, *Loc. cit.*; *Phil. Trans. Roy. Soc.*, p. 236.

If x is measured downwards from the fixed point, the equation of motion is

$$\frac{m\,d^2x}{dt^2} = mg - \tfrac{1}{2}\,\mathrm{E}\left(1 - \frac{l^2}{x^2}\right). \tag{2}$$

Putting $y = x/l$, we have on integration

$$\tfrac{1}{2}\,ml\left(\frac{dy}{dt}\right)^2 = (mg - \tfrac{1}{2}\,\mathrm{E})\,y - \tfrac{1}{2}\,\frac{\mathrm{E}}{y} + \mathrm{C}, \tag{3}$$

C being a constant of integration.

Now the velocity of the particle vanishes at two points in its line of motion. Let these be given by $y = \alpha$ and $y = \beta$ $(\alpha > \beta)$. We can re-write (3) as

$$\tfrac{1}{2}\,ml\left(\frac{dy}{dt}\right)^2 = (\tfrac{1}{2}\,\mathrm{E} - mg)\,\frac{(\alpha - y)\,(y - \beta)}{y}, \tag{4}$$

where

$$\alpha\,\beta = \frac{\mathrm{E}}{\mathrm{E} - 2\,mg}. \tag{5}$$

$\mathrm{T} = mg = \tfrac{1}{2}\,\mathrm{E}$ gives infinite elongation, and hence corresponds to the yield point. Therefore, $mg < \tfrac{1}{2}\,\mathrm{E}$.

From (4) we see that t and y are connected by means of the elliptic integral of the second kind, *viz.*,

$$t = \sqrt{\frac{ml}{\mathrm{E} - 2mg}} \int_y^\alpha \frac{y\,dy}{\sqrt{y\,(\alpha - y)\,(y - \beta)}} \tag{6}$$

Putting $y = \alpha\,(1 - k^2 \sin^2\phi)$, where $k^2\alpha = (\alpha - \beta)$, we get

$$t = 2\,\sqrt{\alpha}\cdot\sqrt{\frac{ml}{\mathrm{E} - 2\,mg}} \int_0^\phi \sqrt{1 - k^2 \sin^2\phi}\;d\phi$$

$$= 2\,\sqrt{\alpha}\cdot\sqrt{\frac{ml}{\mathrm{E} - 2mg}}\;\mathrm{E}\,(k, \phi). \tag{7}$$

But

$$mg = \tfrac{1}{2}\,\mathrm{E}\left[1 - \frac{1}{(1 + \mathrm{L}/l)^2}\right],$$

or

$$\sqrt{\frac{\mathrm{E}}{\mathrm{E} - 2mg}} = 1 + \frac{\mathrm{L}}{l}, \tag{8·1}$$

so that

$$\alpha\,\beta = \left(1 + \frac{\mathrm{L}}{l}\right)^2. \tag{8·2}$$

Putting

$$k^2 = 1 - \frac{\beta}{\alpha} = \sin^2\theta,$$

we get,

$$\alpha = \left(1 + \frac{\mathrm{L}}{l}\right)\sec\theta = \frac{l'}{l}\,\sec\theta, \tag{8·3}$$

and $$\text{Amplitude} = l(\alpha - \beta) = l\left(1 + \frac{L}{l}\right)\sin\theta\tan\theta$$
$$= l' \sin\theta \tan\theta, \qquad (8\cdot4)$$

where l' is the stretched length in the position of equilibrium.

We can now rewrite (7) as

$$t = 2\sqrt{\frac{ml}{E}}\left(\frac{l'}{l}\right)^{\frac{3}{2}}\sqrt{\sec\theta}\,E(k, \phi). \qquad (9)$$

The period of a complete oscillation is, therefore, given by

$$T = 4\sqrt{\frac{ml}{E}}\left(\frac{l'}{l}\right)^{\frac{3}{2}}\sqrt{\sec\theta}\,E_0, \qquad (10)$$

E_0 being the complete elliptic integral of the second kind.

If Hooke's Law is adopted, the period is known to be

$$T_0 = 2\pi\sqrt{\frac{ml}{E}}. \qquad (11)$$

Hence,

$$\frac{T}{T_0} = \frac{2}{\pi}E_0\left(\frac{l'}{l}\right)^{\frac{3}{2}}\sqrt{\sec\theta}. \qquad (12)$$

As the amplitude increases with both θ and l', the ratio (T/T_0) increases with the amplitude.

The variation of $(2/\pi)\,E_0\sqrt{\sec\theta}$ and $\sin\theta\tan\theta$ with respect to θ is given in the following table:

TABLE

θ	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°
$(2/\pi)\,E_0\sqrt{\sec\theta}$	1	1·000	1·001	1·004	1·014	1·037	1·090	1·217	1·589	∞
$\sin\theta\tan\theta$	0	0·031	0·124	0·289	0·539	0·913	1·500	2·582	5·585	∞

It is clear from the table that the period does not vary very much with the amplitude for small values of θ. But this variation cannot be neglected when θ exceeds 40°.

For a given value of θ we see from (12) that

$$(T/T_0)^2 \propto l'^3,$$

which shews that the variation of (T/T_0) with l' follows the law of the semi-cubical parabola.

A REMARK ON g (*n*).

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Received December 2, 1938

§ 1. In my previous note[1] with this title I pointed out that

Theorem

$$\limsup_{x \to \infty} \frac{K(x)}{x} = 1$$

where K (x) *is the number of solutions of*

$$g(n) = 2^n + \left[\left(\frac{3}{2}\right)^n\right] - 2.$$

(Here $[x]$ denotes the greatest integer $\leqslant x$, and $g(n)$ is the least s such that every integer > 0 is a sum of s nth powers of integers $\geqslant 0$) is an easy consequence of known results. The present note contains full details of the proof.

§ 2. Mahler (*Acta Arithmetica*, Band 3, p. 93, theorem 4) proved the

Theorem. *Suppose that* $\theta \neq 0$ *is an algebraic number and that* u *and* v *are integers with* $u > v > 1$, $v \nmid u$, *that* ϵ *is a positive constant, and that* $n = n_1, n_2, n_3, \cdots$ *is an infinite increasing sequence of positive integers for which*

$$\theta\left(\frac{u}{v}\right)^n - \left[\theta\left(\frac{u}{v}\right)^n\right] \leqslant u^{-\epsilon n}.$$

Then

$$\limsup_{t \to \infty} \frac{n_{t+1}}{n_t} = \infty.$$

In this theorem take

$$u = 3, v = 2, \theta = -1, \epsilon = \frac{1}{100}.$$

We shall write

$$3^n = l.\, 2^n + r \quad (0 < r < 2^n).$$

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[1] *Proc. Ind. Acad. Sci.*, Oct. 1938, vol. 8, p. 237.

In that note the word " true " (in the second of the three theorems stated) is to be replaced by " false ".

Further we use $f(x)$ to denote the fractional part of x, and note that if w (> 0) is not an integer, then

$$[-w] = -\{[w] + 1\}.$$

From Mahler's theorem it now follows that, given any $A > 0$, however large, we can find infinitely many integers x such that

$$1 - f\left(\frac{3^n}{2^n}\right) \geqslant \frac{1}{2^{\frac{n}{100}}} \tag{1}$$

is true for $x < n < Ax$.

Now (1) means that

$$f\left(\frac{3^n}{2^n}\right) \leqslant 1 - \frac{1}{2^{\frac{n}{100}}} \tag{2}$$

i.e.,

$$r \leqslant 2^n - 2^{\frac{99n}{100}} \tag{3}$$

Now it is easily verified that for $n > n_0$

$$l + 3 < 2^{\frac{99n}{100}} \tag{4}$$

Hence if (3) is true then, for $n > n_0$,

$$r < 2^n - (l + 3). \tag{5}$$

Thus we conclude that given any $A > 0$, we can find infinitely many x such that (5) is true for $x < n < Ax$.

But Pillai has shown that for $n > n_0$,

$$g(n) = 2^n + \left[\left(\frac{3}{2}\right)^n\right] - 2 \tag{6}$$

if (5) is true. Hence, given any $A > 0$, there exi t infinitely many integers x such that (6) is true for $x < n < Ax$. Thus the theorem stated in § 1 is proved.

REACTIVITY OF THE DOUBLE BOND IN COUMARINS AND RELATED UNSATURATED CARBONYL COMPOUNDS

Part VII. Action of Mercuric Acetate on Hydroxy and 4-Methyl Coumarins

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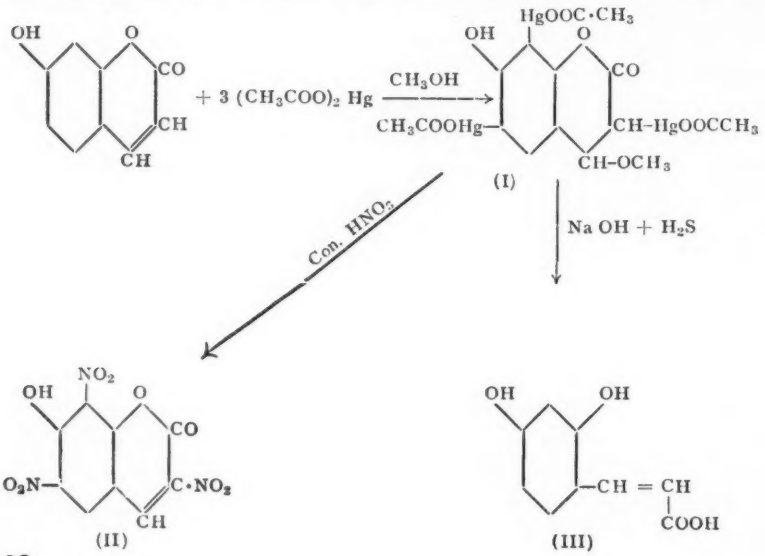
Received November 21, 1938

In continuation of our study of the action of mercury salts on coumarin and substituted coumarins[1] the action of mercuric acetate in methyl alcoholic solution on 7-hydroxycoumarin, 7-hydroxy-4-methylcoumarin and 4 : 7-dimethylcoumarin has now been investigated.

The effect of mercury salts on 7-hydroxycoumarin does not seem to have been studied before. In methyl alcoholic solution, this substance reacts with mercuric acetate rather rapidly to produce a mercuri-compound which is found to be 3 : 6 : 8-triacetoxymercuri-7-hydroxy-4-methoxy melilotic anhydride (I). The constitution is established not only from the



analysis of the compound but also from its conversion by treatment with concentrated nitric acid into 3 : 6 : 8-trinitro-7-hydroxycoumarin (II) identified by comparison with an authentic sample obtained by the direct nitration of umbelliferone.[2] It further gives rise to umbellic acid (III) when hydrogen sulphide is passed into an alkaline solution. The production of a coumaric acid under these conditions clearly indicates that there has been addition at the double bond.[3] Thus umbelliferone behaves like coumarin and 7-methylcoumarin, though its reaction is more vigorous because of the presence of a hydroxyl group in the benzene ring.

Sen and Chakravarti[4] and Naik and Patel[5] studied the action of mercuric acetate on 4-methyl-7-hydroxycoumarin in neutral aqueous medium. Their method involved the opening out of the pyrone ring by dissolving the compound in dilute alkali, neutralising the solution with acetic acid and immediately treating it with an aqueous solution of mercuric acetate. Both the sets of authors noticed that there was dimercuration and the two acetoxymercuri groups were assumed by them to occupy 6 and 8 positions. The reaction has now been carried out in methyl alcoholic solutions. It proceeds very rapidly, producing a monomercuri-compound, the acetoxymercuri group entering position 8. When treated with concentrated nitric acid, this is replaced by a nitro-group and the nitro-compound is found to be identical with 8-nitro-7-hydroxy-4-methylcoumarin obtained by the direct nitration of 4-methyl-umbelliferone.[6] By the action of sodium hydroxide and hydrogen sulphide the original coumarin is obtained and not a coumaric acid, thereby indicating that there has been no addition at the double bond.[3] It is difficult to explain why the reagent has not attacked the double bond because in 4 : 7-dimethylcoumarin with a methyl group in position 4 addition at the double bond is not prevented. The readiness with which position 8 is mercurated is easily understood from analogy with other reactions of 4-methyl-7-hydroxycoumarin which takes up an aldehyde group[7] and a nitro group[6] into position 8 alone under ordinary conditions. A plausible explanation for the entry of only one acetoxymercuri group would be that the high reactivity of position 8 controls the situation. It is substituted first and the resulting compound rapidly gets precipitated owing to its sparing solubility so that no addition at the double bond or further mercuration in position 6 takes place.

Clayton[8] observed that 4 : 7-dimethylcoumarin combined readily with one molecule of mercuric chloride in ether solution. Later Sen and Chakravarti (*loc. cit.*) noticed that when this substance was boiled with mercuric oxide in alkaline solution, a compound containing two mercury atoms was produced. Naik and Patel (*loc. cit.*) studied the action of mercuric acetate

in aqueous medium and reported the occurrence of mono-mercuration which they believed to take place in position 6. In methyl alcoholic solution the reaction proceeds rather slowly and the product obtained is a dimercuri-compound, whose constitution is established as 3 : 6-diacetoxymercuri-4 : 7-dimethyl-4-methoxymelilotic anhydride. It yields 3 : 6-dibromo-4 : 7-dimethylcoumarin when treated with bromine in glacial acetic acid medium. The identity of the bromo-compound is established by comparison with the one obtained by direct bromination of 4 : 7-dimethylcoumarin[9] and by its conversion into 2 : 5-dimethyl-4-bromo-coumarilic acid.[9]

In coumarin and 7-methylcoumarin, besides addition on the double bond, 6- and 8-positions undergo easy mercuration. The introduction of a methyl group in position 4 has a marked influence on the course of the reaction. The double bond still continues to be reactive and addition takes place. Position 6 is obviously more reactive than 8 in 4 : 7-dimethyl-coumarin as could be easily realised from the results of direct bromination[9] and nitration.[10] Only after position 6 has been substituted can position 8 come under the influence of mercuric acetate. Obviously at this stage, that is, as soon as addition at the double bond and mercuration at position 6 are over, the sparingly soluble product separates out and the eighth position escapes mercuration.

With regard to the action of mercuric acetate there are three centres of reactivity in the coumarin molecule :—(1) the pyrone double bond, (2) the position 6, and (3) the position 8. From the results recorded in this series of papers it could be concluded that their relative activity is considerably affected by substituents already present. A hydroxyl group in position 7 seems to enhance markedly the reactivity of (3) as compared with the others and a methyl group in position 4 seems to decrease to some extent the reactivity of (1).

Experimental

Action of Mercuric Acetate.—

(1) *On 7-hydroxycoumarin (umbelliferone) : Preparation of 3 : 6 : 8-triacetoxymercuri-7-hydroxy-4-methoxy-melilotic anhydride.* Umbelliferone (2 g.) and mercuric acetate (12 g.) were dissolved in 10 and 200 c.c. respectively of pure methyl alcohol containing a little acetic acid. The solutions which were quite clear in the cold were mixed together and then raised to the boiling point under reflux. Almost immediately, a brown coloured solid separated out. It was filtered off and discarded and the mother liquor boiled under reflux on a water-bath. Now an almost colourless substance was precipitated gradually and it was collected at intervals. The reaction was practically complete after heating for ten hours. The condensation

product was purified by repeated washing with a cold dilute solution of acetic acid and subsequently with hot methyl alcohol. It was first dried in air and then in a vacuum desiccator. The yield of the pure product which decomposed at 232° was about 7 g. It was almost insoluble in all the ordinary organic solvents and under the microscope it exhibited no definite crystalline structure. (Found : Hg, 61·5 ; $C_{16}H_{16}O_{10}Hg_3$ requires Hg, 62·1 %.) Even when less quantities of mercuric acetate were used (4 or 8 g. of mercuric acetate for every 2 g. of the hydroxycoumarin) the same condensation product was obtained but in diminished yields. In all the cases better yields were obtained by mixing hot saturated solutions of the reactants ; but the purity of the product suffered a good deal.

The mercuri-compound was dissolved in cold 10% sodium hydroxide solution, cooled to 0° with ice and saturated with hydrogen sulphide. The precipitated mercuric sulphide was filtered off and the clear filtrate acidified with dilute hydrochloric acid keeping the temperature at 0° throughout. A slightly brown solid separated out during the acidification. It was filtered, washed with a small quantity of water and crystallised from alcohol. It was completely soluble in sodium bicarbonate solution and was found to be identical with 4-hydroxycoumaric acid (umbellic acid) decomposing at 260° with a little previous sintering.

The condensation product (5 g.) was suspended in concentrated sulphuric acid (20 c.c.) and cooled to −10°. A mixture of fuming nitric acid (15 c.c.) and concentrated sulphuric acid (22 c.c.) was added drop by drop to the suspension keeping the temperature below − 5° and stirring well with an electric stirrer. The addition took about an hour. As the nitric-sulphuric acid mixture was added, the suspension gradually disappeared, and subsequently a yellow substance began to separate out. After stirring for another hour, the contents were poured on to crushed ice. Not much ice could be used, as the nitrocompound was soluble in water to some extent. The yellow solid which separated was filtered and crystallised from benzene as needles melting at 219°–20°. It was identified as 3 : 6 : 8-trinitro-7-hydroxycoumarin by a comparison with an authentic sample prepared by the direct nitration of umbelliferone.

(2) *On 4-methyl-7-hydroxycoumarin* : *Preparation of 8-acetoxy-mercuri-7-hydroxy-4-methylcoumarin.*—The reaction was carried out under the same conditions as with umbelliferone. The condensation took place extraordinarily rapidly and the product separated out within two or three minutes, giving rise to violent bumping. From 2 g. of 4-methyl-7-hydroxycoumarin in 8 c.c. of methyl alcohol and 4 g. of mercuric acetate in 60 c.c. of the same solvent, 4 g. of the condensation product were obtained. It

was purified as in the case of the condensation product from umbelliferone. After drying in the vacuum desiccator, it was found to decompose at 246°. It had no definite crystalline structure and was insoluble in all the ordinary organic solvents, though it easily dissolved in sodium hydroxide without showing any fluorescence (compare 4-methyl-7-hydroxycoumarin which exhibits a beautiful violet fluorescence in alkaline solutions). The same product was obtained even when larger amounts of mercuric acetate were employed. (Found : Hg, 45·5 ; C, 32·7 ; $C_{12}H_{10}O_5Hg$ requires Hg, 46·1 ; C, 33·1%.)

When hydrogen sulphide was passed into an alkaline solution (10% NaOH) of the substance, mercuric sulphide was precipitated along with 4-methyl-7-hydroxycoumarin. The hydroxymethylcoumarin was separated from the mercuric sulphide by extraction with hot alcohol. The alkaline filtrate on acidification gave some more of the 4-methyl-7-hydroxycoumarin melting at 185°.

The condensation product was subjected to the action of nitric acid as in the case of umbelliferone. For 20 g. of the mercuri-compound suspended in 100 c.c. of con. sulphuric acid, a mixture of 12 c.c. of fuming nitric acid and 24 c.c. of concentrated sulphuric acid was used in the first instance and another 18 c.c. of the acid mixture added after stirring for 4 hours. Stirring was continued for one hour more. The yellow solid that separated out on the dilution of the contents with ice-cold water was filtered and crystallised from alcohol. It came down as yellow rhombic plates and was identified as 4-methyl-7-hydroxy-8-nitrocoumarin by comparison with an authentic specimen melting at 256°.

(3) *On* 4 : 7-*dimethylcoumarin* : *Preparation of* 3 : 6-*diacetoxymercuri*-4 : 7-*dimethyl*-4-*methoxy-melilotic anhydride*.—The procedure was just the same as in the previous cases. However, the condensation product did not immediately separate out and the reaction was very slow. From 8 g. of mercuric acetate in 12 c.c. of pure methyl alcohol containing a little acetic acid and 2 g. of 4 : 7-dimethylcoumarin in 100 c.c. of the same solvent, only 0·5 of a g. of a colourless solid separated out after boiling for 40 hours. The mother-liquor on further refluxing gave more and more of the product. The condensation was incomplete even after 100 hours, 3 g. being the amount produced at the end of this period. Purification and drying of the mercuri-compound were effected as already described. It was sparingly soluble in all the ordinary organic solvents and did not possess any definite crystalline structure. It sintered at 233° and decomposed at 242°. (Found : Hg, 55·9 ; $C_{16}H_{18}O_7Hg_2$ requires Hg, 55·5%.) Even when three times the molecular proportion of mercuric acetate were employed, the same product

containing two mercury atoms was obtained. By starting with saturated boiling solutions of the reactants and mixing them, the speed of the reaction and the yield improved but the product was then rather impure.

When a solution of the mercuri-compound in aqueous sodium hydroxide was decomposed with hydrogen sulphide and the clear alkaline filtrate obtained after the removal of the mercuric sulphide was acidified, a colourless crystalline precipitate soluble in sodium bicarbonate solution was obtained. It melted at about 150° with decomposition and was evidently β : 4-dimethylcoumaric acid. It underwent change slowly into 4 : 7-dimethylcoumarin when allowed to remain in contact with mineral acids and very rapidly when boiled with alcohol for purposes of crystallisation. This peculiar rapid ring closure is evidently due to the presence of a methyl group in the β-position in the coumaric acid.[11]

The mercuri-compound was suspended in glacial acetic acid and treated with a solution of bromine in the same solvent with vigorous shaking. The colour was rapidly discharged and the suspension disappeared. More bromine was added in small quantities at a time till the colour just persisted after shaking. Gradually the bromo-compound separated out, along with a little mercuric bromide. The precipitation was completed by adding excess of water and the solid was collected. The bromo-compound could be freed from the accompanying mercuric bromide by repeated crystallisations from glacial acetic acid. Another method of effecting the separation was to treat the mixture with 20% sodium hydroxide when the bromo-compound went into solution, leaving behind mercury in the form of the oxide. Acidification of the clear filtrate reprecipitated the bromo-compound in a pure condition. It crystallised from alcohol as long rods with rectangular sides and melted at 220°. Its identity with 3 : 6-dibromo-4 : 7-dimethylcoumarin was established by a comparison with an authentic sample.[9] (Found : Br, 47·8 ; $C_{11}H_8O_2Br_2$ requires Br, 48·2%.)

The identity of the bromo-compound was further confirmed by its conversion into 2 : 5-dimethyl-4-bromocoumarilic acid. 2 g. were refluxed for 3 hours with 50 c.c. of alcohol containing 4 g. of potassium hydroxide. On dilution of the clear solution with water and subsequent acidification, a colourless precipitate was obtained. It was completely soluble in sodium bicarbonate. A very dilute solution of the bicarbonate should be used, as otherwise the sparingly soluble sodium salt of the coumarilic acid gets precipitated. The substance could be easily crystallised from glacial acetic acid or alcohol in the form of rectangular plates melting at 273°. The silver salt was obtained as a colourless solid. (Found : Ag, 28·8 ; $C_{11}H_8BrO_3$ Ag requires Ag, 28·7%.) This bromocoumarilic acid was compared and found

to be identical with 2 : 5-dimethyl-4-bromocoumarilic acid obtained from 3 : 6-dibromo-4 : 7-dimethyl coumarin.[9] It should be noted that the above coumarilic acid melts at 273° and not at 225° as stated by previous workers.

Summary

The action of mercuric acetate in methyl alcoholic solution on (1) umbelliferone, (2) 4-methylumbelliferone and (3) 4 : 7-dimethylcoumarin has been investigated. With umbelliferone addition at the double bond and substitution in positions 6 and 8 take place whereas in the case of its 4-methyl derivative position 8 alone is mercurated to yield a monoacetoxymercuri-compound. In regard to the last compound the reaction stops with addition at the double bond and mercuration of the 6th position, the position 8 escaping the attack of the reagent. It is concluded that owing to the influence of the substituent groups the reactivity of the three active centres of the coumarin molecule are differently affected.

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ON WARING'S PROBLEM WITH POWERS OF PRIMES

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Received December 13, 1938
(Communicated by Prof. A. Narasinga Rao)

Let k be any integer $\geqslant 4$ and p^θ be the highest power of the prime p which divides k.

Let

$$\gamma = \begin{cases} \theta + 2 \text{ for } p = 2,\ 2 \mid k, \\ \theta + 1 \text{ otherwise} \end{cases}$$

and

$$K = \prod_{(p-1)\mid k} p^\gamma$$

Then Loo-keng Hua* proves

Theorem. *Every sufficiently large integer* $N \equiv s$ *(mod. K) is a sum of* s k*th powers of primes, provided* $s \geqslant s_0$, *where* $s_0 = s_0(k) \sim 6k \log k$.

Towards the end of the paper, he remarks " The congruence condition in the theorem is essential and cannot be replaced by a weaker one. "

Let $G_1(k)$ be the least value of s such that every large integer is the sum of at most s kth powers of *primes*.

Then Hua's result means that

$$G_1(k) \leqslant K + s_0.$$

It can be proved that, for an infinite number of values of k, K is greater than any power of k. So from Hua's result we cannot derive that $G_1(k)$ is less than some fixed power of k for all k. The object of this paper is to derive from Hua's result, that

$$\overline{\lim_{k \to \infty}} \frac{G_1(k)}{k \log k} \leqslant 6.$$

Further Notations

Let $K = 2^\gamma \cdot p_1^{\gamma_1} p_2^{\gamma_2} \cdots p_n^{\gamma_n}$ so that $\gamma_r = \theta_r + 1$ and $p_r^{\theta_r} \parallel k$, and $(p_r - 1) \mid k$, for $r = 1, 2, \cdots n$.

Further let $d_r = p_r^{\gamma_r}$, $r = 1, \cdots, n$.

P is the smallest prime which does not divide K.

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* *Mathematische Zeitschrift*, 1938, **44 Band**, 3 Heft, 334–46.

$t = t(k)$ is the least value of s such that $N \equiv x_1 + \cdots + x_s \pmod{K}$ is solvable for ever N in terms of x, where

$$x = 0, P^k \text{ or } p^k, \text{ where } p \mid K$$
$$T = 2(d_1 + \cdots + d_n) + 2^\gamma - 2n + 1$$
$$T_0 = 3(d_1 + \cdots + d_n) + 2^\gamma - 2n.$$

$A_1, A_2, \cdots, A_u$ denote the different positive reduced residue classes mod. K, in $x_1 p_1^k + x_2 p_2^k + \cdots + x_n p_n^k$ where $1 \leqslant x_r \leqslant d_r$, $r = 1, \cdots, n$, arranged in ascending order of magnitudes.

$$J = [(d_1 + d_2 + \cdots + d_n - n + 1)/2^\gamma].$$

Lemmas

Lemma (1): *If* $(hA, B) = 1$, *then we can find* x, y *such that*

$$hA\,x + By \equiv C \pmod{AB},$$

with $1 \leqslant x \leqslant B$ *and* $1 \leqslant y \leqslant A$, *where* h, A, B, C *are given.*

Since $(h\,A, B) = 1$, when $x = 1, 2, \cdots, B$ and $y = 1, 2, \cdots, A$, $hAx + By$ takes incongruent values mod. AB. Hence it runs through a complete residue system mod. AB.

So the lemma follows:

Lemma (2): *Let* $(h_s, d_s) = 1, s = 1, \cdots, n$ *and* C *be any integer. Then we can find* X_s *such that* $1 \leqslant X_s \leqslant d_s, s = 1, \cdots, n$, *and* $X_1 h_1 d_2 \cdots d_n + X_2 h_2 d_1 d_3 \cdots d_n + \cdots + X_n h_n d_1 \cdots d_{n-1} \equiv C \pmod{d_1 \cdots d_n}$.

Since $d_1, \cdots, d_n$ are prime to one another, $(d_1, h_1 d_2 \cdots d_n) = 1$. So by lemma (1), we can find X_1, Y_1 such that

(1) $h_1 d_2 \cdots d_n X_1 + d_1 Y_1 \equiv C \pmod{d_1 d_2 \cdots d_n}$ with $1 \leqslant X_1 \leqslant d_1$ and $1 \leqslant Y_1 \leqslant d_2 \cdots d_n$.

Again by lemma (1), we have

(2) $h_2 d_3 \cdots d_n X_2 + d_2 Y_2 \equiv Y_1 \pmod{d_2 \cdots d_n}$, with $1 \leqslant X_2 \leqslant d_2$, $1 \leqslant Y_2 \leqslant d_3 \cdots d_n$.

Hence from lemma (2), we get

(3) $h_3 d_4 \cdots d_n X_3 + d_3 Y_3 \equiv Y_2 \pmod{d_3 \cdots d_n}$ with $1 \leqslant X_3 \leqslant d_3$, $1 \leqslant Y_3 \leqslant d_4 \cdots d_n$.

By repeating this we get,

$h_{n-1} d_n X_{n-1} + d_{n-1} Y_{n-1} \equiv Y_{n-2} \pmod{d_{n-1} d_n}$, with $1 \leqslant X_{n-1} \leqslant d_{n-1}$, $1 \leqslant Y_{n-1}, \leqslant d_n$.

Finally, we have

$$h_n X_n \equiv Y_{n-1} \pmod{d_n}$$

with $1 \leqslant X_n \leqslant d_n$.

By multiplying the second congruence by d_1, the third by $d_1 d_2, \cdots$, and the last by $d_1 d_2 \cdots d_{n-1}$, we get

$$\begin{aligned}
&h_1 d_2 \cdots d_n X_1 + d_1 Y_1 \equiv C \pmod{d_1 \cdots d_n}\\
&h_2 d_1 d_3 \cdots d_n X_2 + d_1 d_2 Y_2 \equiv d_1 Y_1 \quad (\ ,,\ )\\
&h_3 d_1 d_2 d_4 \cdots d_n X_3 + d_1 d_2 d_3 Y_3 \equiv d_1 d_2 Y_2 \quad (\ ,,\ )\\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
&h_{n-1} d_1 \cdots d_{n-2} d_n X_{n-1} + d_1 \cdots d_{n-1} Y_{n-1} \equiv d_1 \cdots d_{n-2} Y_{n-2} \quad (\ ,,\ )\\
&h_n d_1 \cdots d_{n-1} X_n \equiv d_1 \cdots d_{n-1} Y_{n-1} \quad (\ ,,\ )
\end{aligned}$$

By adding all the above and cancelling common terms, we get the lemma.

Lemma (3): *When* $r = 1, 2, \cdots, n$, $p_r^k \equiv h_r \cdot \dfrac{K}{d_r} + 1 \pmod{K}$, *where* $(h_r, d_r) = 1$.

By Fermat's theorem

$$p_r^k \equiv 1 \pmod{p_s},\ s = 1, \cdots, r-1, r+1, \cdots, n.$$

Further

$$p_r^k \equiv 1 \pmod{2^\gamma}.$$

Hence $$p_r^k \equiv 1 \pmod{K/d_r}.$$

Hence $$p_r^k \equiv h_r \cdot \frac{K}{d_r} + 1 \pmod{K}.$$

Since $(p_r^k, K) = d_r$, $(h_r, d_r) = 1$.

Lemma (4): $A_r - A_{r-1} \leqslant T$, $r = 2, 3, \cdots, u$

and $$K + A_1 - A_u \leqslant T.$$

In lemma (2), put $C = J + 1$ and h_r equal to the h_r defined in lemma (8) and multiply throughout by 2^γ. Then we get

$$X_1 h_1 K/d_1 + \cdots + X_n h_n K/d_n \equiv C \cdot 2^\gamma \pmod{K}.$$

Let $A_r \equiv a_1 p_1^k + \cdots + a_n p_n^k \pmod{K}$ with $1 \leqslant a_s \leqslant d_s$ $s = 1, \cdots, n$.

Then

$$\begin{aligned}
A_r - C\,2^\gamma &\equiv \sum_{s=1}^{n} a_s p_s^k - C \cdot 2^\gamma \pmod{K}\\
&\equiv \sum_{s=1}^{n} a_s \left(h_s \frac{K}{d_s} + 1\right) - \sum_{s=1}^{n} X_s h_s \frac{K}{d_s} \pmod{K}\\
&= \sum_{s=1}^{n} (a_s - X_s) h_s K/d_s + a_1 + \cdots + a_n.
\end{aligned}$$

Let $a_s - X_s \equiv b_s \pmod{d_s}$,

where $1 \leqslant b_s \leqslant d_s$.

Then $(a_s - X_s)\, h_s\, K/d_s \equiv b_s h_s\, K/d_s \pmod{K}$.

Hence

$$A_r - C\,2^\gamma \equiv \sum_{s=1}^{n} \{(b_s\, h_s\, K/d_s) + a_s\} \pmod{K}$$

$$= \sum_{s=1}^{n} \left\{ b_s \left(h_s \frac{K}{d_s} + 1 \right) + a_s - b_s \right\}$$

$$\equiv \sum_{s=1}^{n} b_s\, p_s^k + \sum_{s=1}^{n} (a_s - b_s) \pmod{K}$$

Let $\sum_{s=1}^{n} b_s\, p_s^k \equiv A_i \pmod{K}$.

Then

$$A_r - A_i \equiv C \cdot 2^\gamma + \sum_{s=1}^{n} (a_s - b_s) \pmod{K}.$$

Now

$$C\,2^\gamma + \sum_{s=1}^{n} (a_s - b_s) \leqslant (J+1)\,2^\gamma + \sum_{s=1}^{n} (d_s - 1)$$

$$\leqslant d_1 + \cdots + d_n - n + 1 + 2^\gamma + d_1 + \cdot + d_n - n$$

$$= 2 \sum_{r=1}^{n} d_r + 2^\gamma - 2n + 1$$

Again

$$C\,2^\gamma + \sum_{s=1}^{n} (a_s - b_s) \geqslant (J+1)\,2^\gamma + \sum_{s=2}^{n} (1 - d_s)$$

$$\geqslant d_1 + \cdot + d_n - n + 1 + n - (d_1 + \cdot + d_n)$$

$$= 1.$$

So

$$A_r - A_i \equiv D \pmod{K}$$

where $1 \leqslant D \leqslant T$.

This means that $r \neq i$, and

$$1 \leqslant A_r - A_i \leqslant T \text{ when } i < r$$

and

$$1 \leqslant K + A_r - A_i \leqslant T \text{ when } i > r.$$

From this the lemma follows :

Lemma (5) : $t = t(k) \leqslant T_0$.

Let $1 \leqslant S \leqslant K$. Then, by lemma (4),

if $A_r < S \leqslant A_{r+1}$, $1 \leqslant S - A_r \leqslant A_{r+1} - A_r - 1 \leqslant T - 1$,

and if $A_u < S \leqslant K$, $1 \leqslant S - A_u \leqslant K - A_u - 1 \leqslant T - 1$.

Hence if $1 \leqslant S \leqslant K$, there is one r such that

$1 \leqslant S - A_r \leqslant T - 1$, where $r = 0, \cdots, u$, and $A_0 = 0$.

So $S = A_r + D$ where $D \leqslant T - 1$.

For every N there is one S such that

$$1 \leqslant S \leqslant K \text{ and } N \equiv S \text{ (mod. K)}.$$

But $S = A_r + D$.

Hence $N \equiv A_r + D$ (mod. K).

Further

$$D \equiv D \cdot P^k \text{ (mod. K)}$$

and

$$A_r \equiv a_1 p_1^k + \cdots + a_n p_n^k \text{ (mod. K)}$$

where $1 \leqslant a_s \leqslant d_s$, $s = 1, \cdots, n$.

So

$$N \equiv a_1 p_1^k + \cdots + a_n p_n^k + D \cdot P^k \text{ (mod. K)}.$$

Since $a_1 + \cdot + a_n \leqslant d_1 + \cdots + d_n$

and $D \leqslant T - 1$, the lemma follows.

Lemma (6) : $T_0 \leqslant 4 \cdot 5\, \sigma(k) + 4k$,

where $\sigma(k) = \sum_{d \mid k} d$.

$$T_0 = 3 \sum_{r=1}^{n} d_r + 2^\gamma - 2n$$

$$= 3 \Sigma p^{\theta+1} + 2^\gamma - 2n, \text{ where } p \text{ is an odd prime such that } (p-1)\, p^\theta \mid k.$$

So

$$T_0 = 3 \Sigma \frac{p}{p-1} (p-1)\, p^\theta + 2^\gamma - 2n$$

$$\leqslant 3 \Sigma \tfrac{3}{2} (p-1)\, p^\theta + 2^\gamma$$

$$\leqslant 4 \cdot 5 \sum_{d \mid n} d + 4k$$

$$= 4 \cdot 5\, \sigma(k) + 4k.$$

Theorems

THEOREM I : $G_1(k) \leqslant s_0 + t$.

From the definition of t, for every N

$$N - s_0 \equiv x_1 + x_2 + \cdots + x_t \text{ (mod. K)}.$$

where $x = 0$, P^k, or p^k, where $p \mid K$.

Let $M = N - x_1 - \cdots - x_t$.

Then M is large when N is large and $M \equiv s_0$ (mod. K).

Therefore from Hua's result, M is the sum of s_0 kth powers of primes.

But $N = M + x_1 + \cdot + x_t$, where $x = 0$, P^k or p^k.

Hence N is the sum of at most $s_0 + t$ kth powers of primes.

THEOREM II. $G_1(k) \leqslant s_0 + T_0$.

This follows from Theorem I and lemma (5).

THEOREM III. $G_1(k) \leqslant s_0 + 4 \cdot 5\,\sigma(k) + 4k$.

This follows from Theorem II and lemma (6).

THEOREM IV. $\lim_{k \to \infty} \frac{G_1(k)}{k \log k} \leqslant 6$.

Since $T_0 = 0$ $[\sigma(k)]$ and $s_0 \backsim 6k \log k$, the theorem follows from Theorem III.

THEOREM V. $G_1(4) \leqslant 34$.

By verification $t = 15$, when $k = 4$ and $s_0 = 19$.

THEOREM VI. $G_1(6) \leqslant 56$.

By verification $t(6) = 11$, and $s_0(6) = 45$.

Conclusion

Conjecture I. $t(k) \leqslant \Gamma(k) + 2$ in all cases, except when $k = 2$.

Elsewhere, I have shown that when $k = 2^r$ or $\phi(p^\theta)$

$$G_1(k) \geqslant \Gamma(k) + 2, \text{ and } G_1(2) \geqslant 7.$$

By slightly modifying the method of proof for lemma (2), we can prove

THEOREM: *If* $(a_1, a_2, \cdots, a_n) = 1$

we can find $x_1, \cdots, x_n$ *integers such that*

$$|x_r| < (a_1, a_2, \cdots, a_{r-1}, a_{r+1}, \cdots, a_n), \quad r = 1, \cdots, n$$

and $a_1 x_1 + a_2 x_2 + \cdots + a_n x_n = 1$.

DIAMAGNETISM OF SOME ORGANIC LIQUID MIXTURES

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Received September 29, 1938

1. *Introduction*

A large amount of work has been accomplished recently on the magnetic susceptibility of binary mixtures of organic and inorganic liquids.[1] Unfortunately reports are not unanimous regarding the behaviour of such mixtures from the point of view of the additive law of magnetic susceptibilites. Certain general tendencies however are sufficiently clear, but the detailed results of different authors differ considerably.

Trew and Spencer[2] undertook more recently a careful study of the changes in physical properties of binary mixtures when their composition was varied. They measured the density, refractive index, heat of mixing, specific heat, and magnetic mass susceptibility of a series of binary mixtures of the liquids : benzene, toluene, *m*-cresol, aniline and nitrobenzene. Nitrobenzene-*m*-cresol mixtures showed the least deviation from the additive law. None of the other pairs of liquid mixtures could be considered ideal. They could not obtain any general rule to govern the deviations, but they have observed that the magnetic mass susceptibility proves a more nearly additive property than any other property investigated.

A careful and thorough investigation on the magnetic susceptibilities of binary mixtures of some organic liquids has been carried out by Seely.[3] Benzene-nitrobenzene mixtures followed the additivity law in the range of temperature 10°–50° C. For mixtures of carbon tetrachloride with either benzene or nitrobenzene, a systematic deviation from additivity was found. The deviations for both the groups showed a definite dependence upon concentration and temperature.

At the same time, solutions of salts in water have also been examined carefully and we have very reliable results on this subject. Ikenmeyer[4] studied the solutions of alkali halides in water and calculated the ionic susceptibilities of the alkali and halogen ions. Farquharson[5] and Scott and Blair[6] found small deviations from linearity in the case of some alkali halides. Hocart[7] examined a number of halides and obtained results for dissolved

salts at 30 to 60% concentration. He found that the susceptibility of the dissolved salts as calculated from an application of the additivity law to the solutions, was 2–3% higher than the susceptibility for the corresponding solid salts.

Hoare and Brindley[8] have recently determined the susceptibility of salts composed of ions with inert gas configurations and found that in the halides of lithium and caesium the additivity law breaks down. Flordal and Frivold[9] obtained large changes of susceptibility when some alkaline earth halides were dissolved in water. Similar results were also recorded by Subramaniam[10] who discussed the magnetic effects accompanying ionic deformations in the solid salts studied. Varadachari[11] had previously drawn attention to such effects in his study of sulphuric acid-water mixtures. He investigated also acetic acid-water mixtures and obtained no departure from the additive law.

Investigations by Rao and Sriraman[12] have shown that when some salts are dissolved in water, departures from the additivity law may be observed. In these cases, the percentage changes appear to be independent of concentration and have been attributed to (1) interaction between the ions and water molecules, (2) depolymerisation of water, (3) release of constraints within the molecules due to their breakage into ions and (4) change of valency of any of the ions when the salt is dissolved. While the first two causes do not produce more than 1% change from the additive law, the other two causes give rise to much larger changes.

Stoner[13] has presented a clear account of the possible theoretical support for such deviations. He has suggested that some of these deviations could be attributed to the hydration of ions. The enormous electric fields at molecular distances round an ion are sufficient to orientate water molecules. It would be expected that such a close association of the water molecules with ions will bring about a reduction in the diamagnetism of water.

A straight inference from this discussion leads one to expect that molecules having large electrical moments would give rise to a large interaction with other molecules also having large electric moments. The exact operation of such inter-molecular interactions is uncertain in the present state of our knowledge of the subject but the investigations of Trew and Spencer[2] and Seely[3] suggest small changes in diamagnetic susceptibility due to these causes.

It was believed, therefore, that a careful examination of the diamagnetism of some binary mixtures of organic liquids, whose molecules carry a large dipole moment, might be of interest. Thorough purification of the liquids

studied and the adoption of a magnetic method which could give consistent results were the guiding features of the investigation. The density and refractive index of the mixtures have also been carefully studied.

In this investigation, the diamagnetic susceptibility of binary mixtures of formic acid and acetic acid with ethyl alcohol, methyl alcohol, acetone, water and ethyl ether have been studied. The liquids have been purified with the greatest care and in accordance with standard methods. The Gouy method has been perfected to give thoroughly reliable results and corrections have been introduced for the partial pressure of the air above the liquids in the containing tube.

2. *Experiment*

(*a*) *Purification of Liquids.*

(i) *Formic acid.*—Formic acid when kept at room temperature slowly decomposes into carbon monoxide and water, the percentage purity being thereby lowered. A freshly opened bottle of formic acid received from Kahlbaum was found to contain 1·5 % of water as determined from the melting point. The purification of the acid was conducted by the method of Coolidge.[14]

Kahlbaum formic acid was thrice distilled under reduced pressure (about 1 cm.), the collecting reservoir being cooled in ice. Each time about 10 % on either side of the distillation was neglected. The formic acid thus purified was solidified in ice, the melting point of the acid being 8·35° C. The solid thus obtained was kept at 5° C. and suction was applied for eight hours, the pressure being 2–3 mm. to remove traces of water in the acid. The purified acid was always kept in the solid state in a refrigerator to avoid decomposition of the acid into carbon monoxide and water and the consequent reduction in the percentage purity.

(ii) *Ethyl alcohol.*—500 c.c. of Merck's absolute alcohol (99%) pure was treated with freshly cut pieces of sodium (4 gr.) and 12 gr. of ethyl phthalate and refluxed for one hour. It was then distilled, the initial and final fractions (10%) being neglected.

(iii) *Methyl alcohol.*—Merck's methyl alcohol was found to be only 98% pure. The method of purification was after Lund and Bjerrum.[15] To 10 c.c. of the methanol, 1 gr. of magnesium cuttings and 1 gr. of iodine were added and the contents refluxed for an hour. 200 c.c. of the original methanol was next added and distilled fractionally. The methyl alcohol thus obtained was 100% pure.

(iv) *Acetone.*—Acetone was dried over anhydrous potassium carbonate, decanted and fractionally distilled.

(v) *Ethyl ether.*—De Hahn's ether was dried over anhydrous calcium chloride decanted and left over excess of sodium wire for 15 days. The ether was next decanted and distilled.

(vi) *Acetic acid.*—The purification of this acid was effected by the method of Orton and Bradfield.[16] The melting point of the available Kahlbaum specimen was 15·6° C. One hundred per cent. acid melts at 16·7° C. It is found that the melting point is lowered by 0·2° C. for every 0·1 per cent. of water. The Kahlbaum specimen therefore should have contained 0·55 per cent. of water. To oxidize any impurities that may be present in the specimen, chromic anhydride was used. But chromic anhydride itself interacts with acetic acid to give water. A 100% sample of acetic acid when distilled with chromic anhydride will melt only at 16·2%, thus indicating the production of 0·25% of water. During the purification excess of acetic acid was added to chromic anhydride and the mixture was kept near the boiling point for half an hour and then fractionally distilled neglecting initial and final fractions. The sample thus obtained was found to have a freezing point 16·4° C. indicating that the acetic acid was 99·85% pure.

(vii) Water was purified, by repeated distillation in an all-glass apparatus.

(*b*) *Determination of Specific Susceptibility.*

The specific susceptibility was determined by the Gouy method. The pole faces of the Pye electromagnet were 3 cm. in diameter and the air gap had a width of 1·2 cm. Measurements of the field strengths were made at different field currents by using a search coil. Water was used as the standard substance. The experimental tube was about 30 cm. long and had an internal diameter of 0·8 cm. It was sealed at one end and in some early experiments a ground stopper was used at the other end. Due however to slow evaporation, the weight of the tube decreased gradually. This decrease proved a source of trouble. It was therefore considered desirable to have a tube similar to the one shown in Fig. 1. AB is about 30 cm. long. The end A is sealed. A narrow tube about 4 mm. internal diameter is connected at B. The tube is cleaned thoroughly and dried. A mark is made exactly midway between A and B. The liquid to be investigated is poured in the tube until its surface is at the mark. The tube is now sealed off at D and the glass drawn in the form of a hook to enable us to suspend the tube from the balance. Hence in the space above the liquid we have air and the saturated vapour of the liquid at the room temperature.

The tube was filled up to the mark M with water and the Gouy force determined at different field currents. The tube was suspended from one

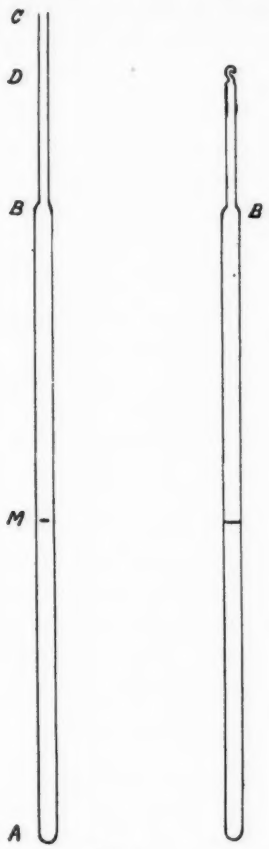

FIG. 1

arm of a chemical balance by a long thin wire. It was arranged to be vertical with the liquid surface symmetrically situated between the pole-pieces. The tube was now counterpoised by placing weights in the other pan. On introducing the magnetic field, the pull on the liquid increases the apparent weight of the tube. Thus the increase in load necessary to counterpoise the tube gives us the Gouy force on the tube.

Since the lengths of glass above and below the water surface are nearly equal, the Gouy force on the tube may be taken to be completely compensated. The observed Gouy force on the tube gives us the force on the water column.

If k_w is the volume susceptibility of water, H the field strength and A the area of cross-section of the water column, the Gouy force m_g is given by

$$mg = \tfrac{1}{2}k_w \, AH^2.$$

We neglect here the field at the lower end of the water column since the column is 15 cms. long. The space above the water contains air and saturated water vapour. If P is the atmospheric pressure and p the saturation vapour pressure of water at the room temperature, $P - p$ gives the residual air pressure. The force on the tube due to the vapour of the liquid could be worked out by assuming the molecular susceptibility to be the same in the liquid and vapour state. On calculation, it was found that the Gouy force even on the vapour of ether was definitely less than 0·5 mg. Since the Gouy forces could be measured only to this order of accuracy, the influence of vapour pressure has been neglected in this investigation. But the residual air in the space above the liquid must be taken into account. Its pressure is $P - p$. If k_a is the volume susceptibility of air at the room temperature and atmospheric pressure P, we have the Gouy force on the residual air equal to $\frac{1}{2}k_a.A.H^2.\frac{P-p}{P}$. Since air is paramagnetic, this force will act in the same direction (downwards) as the force on the liquid. Knowing the saturation vapour pressure for water from the tables and assuming $k_a = +0{\cdot}029$*[17] (paramagnetic) we can calculate the Gouy force on the residual air at different field strengths. In the following table, the corrected Gouy forces on water at different field strengths are deduced.

TABLE I

Field current in amps.	Field in kilogauss	Gouy force on water in mg.	Gouy force on the air above in mg.	Corrected Gouy force on water
3	10·86	21·90	0·9	21·00
4	12·28	27·65	1·0	26·65
5	13·31	32·45	1·2	31·25
6	14·20	36·95	1·4	35·55

When any other liquid is used in place of water, the Gouy force can be corrected if the saturation vapour pressure of the liquid is known at the

* All susceptibility values in this paper are given in 10^{-6} units and are diamagnetic unless otherwise stated.

room temperature. It will be noted that this correction becomes considerable if we take liquids like ethyl ether for which the saturation vapour pressure at room temperature is very large.

Let $m_w g$ and $m_l g$ be the corrected Gouy forces in the case of water and any given liquid when the tube is filled successively with them. For the same field current,

$$m_w g = \tfrac{1}{2} k_w A H^2$$

$$m_l g = \tfrac{1}{2} k_l A H^2$$

$$\therefore \quad \frac{m_l}{m_w} = \frac{k_l}{k_w}.$$

Hence

$$k_l = k_w \cdot \frac{m_l}{m_w}.$$

If the density ρ of the liquid is known, k_l/ρ gives the specific susceptibility of the liquid.

The mixtures were prepared by weighing desired quantities of the two component liquids and mixing them. After filling half the tube with any mixture, it was found better to seal it at atmospheric pressure instead of in vacuum. For when the pump was applied, there was considerable evaporation in the case of volatile liquids and the concentrations of the mixtures varied considerably. A redetermination of the concentration became essential. Hence we preferred to leave air inside the tube when it was sealed and apply a correction for the Gouy force on the residual air inside.

(c) *Determination of Relative Density, Refractive Index and Saturation Vapour Pressure.*

By the hydrostatic method, ρ^l_{32}/ρ^w_{32}, *i.e.*, the ratio of the density of the liquid at 32° C. to the density of water at the same temperature was determined. It is well known that $\rho^w_{32} = 0{\cdot}9951\ \rho^w_4$. Hence the relative density of the liquid which is actually measured is $\rho^l_{32}/0{\cdot}9951\ \rho^w_4$. If this equals d, then the relative density with respect to water at 4° C. will be given by ρ^l_{32}/ρ^w_4 which equals $0{\cdot}9951 \times d$. In the following measurements, the relative densities of the liquids are given in terms of the density of water at 4° C. But in the calculation of the diamagnetic susceptibility, the relative densities calculated in terms of the density of water at 32° C. have been used.

The refractive index of the liquids was measured with an Abbe refractometer of Hilger.

The saturation vapour pressure was found by allowing the liquid to evaporate in a closed evacuated vessel and measuring the pressure with a mercury column. (See for example Findlay's *Practical Physical Chemistry*, p. 66.)

3. *Results*

(*a*) *Pure Liquids.*—

In Table II are given the collected values of the density, specific susceptibility, vapour pressure at room temperature and refractive index of the liquids investigated. The results obtained by other investigators are also given for comparison.

TABLE II

Liquid	Electrical moment of the molecules ($\times 10^{18}$)	Relative density ρ	Ref. index μ	Vapour pressure in cm. of mercury at 32° C.	Specific susceptibility χ
Water	1·85	0·9951	1·3330	3·6	0·720
Formic acid	1·2	1·2070 1·2073* (32° C.)	1·3722 1·3714*	5·8*	0·433 0·432* 0·446§ 0·434¶
Acetic acid	1·4	1·036 1·036* (32°C.)	1·3733 1·3715*	2·4*	0·525 0·526* 0 537† 0·534¶
Methyl alcohol	1·68	0·7903 0·7917* (20° C.)	1·3317 1·3312*	17·8*	0·664 0·650* (−3° C.) 0·697¶
Ethyl alcohol	1·70	0·7812 0·7808* (30° C.)	1·3630 1·3624*	8·6*	0·732 0·744* 0·749¶
Acetone	2·80	0·7805 0·7846* (25° C.)	1·3582 1·3589*	31·0*	0·572 0·581* 0·579† 0·595‡ 0·593¶
Ethyl ether	1·12	0·6984 0·7010* (32° C.)	1·3510 1·3542*	69·0*	0·754 0·766* 0·766¶

* *Int. Crit. Tables.* ‡ Rao and Sivaramakrishnan.[19] ¶ Kido.[21]
† Rao and Varadachari.[18] § Rao and Sriraman.[20]

It will be observed that the values of the relative density, refractive index and specific susceptibility obtained here agree very closely with those of other investigators.

(*b*) *Formic Acid-Water Mixtures.*—

This mixture was studied by Kido.[21] He obtained a close adherence to the law of additivity. Rao and Sriraman[20] also investigated this mixture. The results suggest the formation of a monohydrate of formic acid at a concentration of nearly 70% of the acid. They have suggested an alternative explanation. Formic acid has a molar susceptibility of 20·5 while the formate ion has only a susceptibility of 17·3. The highest value for the acid in the pure state indicates the probable existence of double molecules. But it is uncertain how the association of molecules would give rise to such large changes in susceptibility.

The results obtained here are given in Table III.

TABLE III

% of Formic acid in mixture	Vapour pressure	ρ (32° C.)	ρ (30° C.) (I. C. T.)	μ	χ_1 observed	χ_2 calculated	$\chi_2 - \chi_1$
100	5·8 cm.	1·207	1·2073	1·3722	0·433	0·433	0·000
90	4·1 ,,	1·191	1·1927	1·3726	0·458	0·461	0·003
80	3·3 ,,	1·171	1·1737	1·3692	0·484	0·490	0·006
70	3·0 ,,	1·151	1·1530	1·3661	0·511	0·519	0·008
60	2·8 ,,	1·128	1·1310	1·3620	0·541	0·548	0·007
50	3·0 ,,	1·109	1·1098	1·3584	0·566	0·577	0·011
40	3·1 ,,	1·086	1·0876	1·3546	0·598	0·605	0·007
30	3·2 ,,	1·064	1·0654	1·3514	0·628	0·634	0 006
20	3·3 ,,	1 042	1·0427	1·3471	0·664	0·664	0·000
10	3·6 ,,	1·020	1·0197	1·3420	0·687	0·691	0·004
0	3·6 ,,	0·9951	0·9951	1·3330	0·720	0·720	0·000

A scrutiny of the table shows that in no case is the observed value larger than the calculated value. In most of the cases, the observed value is less than the calculated value. That the variation is systematically positive is significant. As a result of mixing formic acid with water, there is a small but definite decrease in the specific diamagnetic susceptibility. The same observation was made by Rao and Sriraman. Their results also show that the observed values are less than the calculated values. But in their case, the variations were much larger although there is good agreement between our density values.

It is also significant that the departure of the observed specific susceptibility from the calculated value also shows a systematic variation. When we judge the absolute values of $\chi_2 - \chi_1$, it should be remembered that there is likelihood of errors not exceeding 0·3% being present in the observed values. Even making allowance for this error, it will be observed that the difference becomes maximum at about 70% of the formic acid. This result is in accord with the conclusion of Rao and Sriraman.

In Fig. 2 are shown the graphs between concentration and the physical quantities investigated. The density curve also shows a small variation,

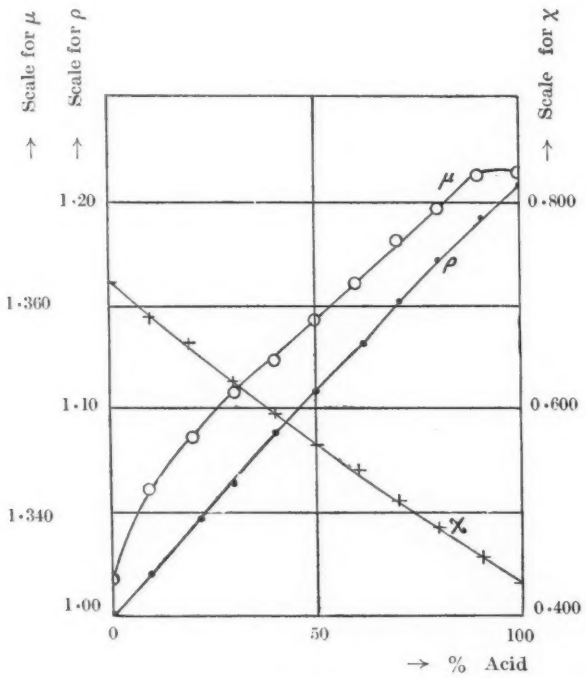

FIG. 2

the observed values being larger than the additive values. A careful examination shows that this variation reaches the maximum value of nearly 1% at 70% concentration of formic acid. The refractive index curve shows a large variation from additivity and there is no correlation between the variations in this case and in the other two cases.

(*c*) *Formic Acid-Methyl Alcohol Mixtures.*—

The results obtained are shown in Table IV.

TABLE IV

% of Formic acid in mixture	ρ	μ	χ_1 observed	χ_2 calculated	$\chi_2 - \chi_1$
100	1·207	1·3722	0·433	0·433	0·000
90	1·146	1·3663	0·452	0·456	+0·004
80	1·086	1·3609	0·482	0·482	0·000
70	1·042	1·3554	0·503	0·503	0·000
60	0·997	1·3514	0·530	0·526	−0·004
50	0·956	1·3479	0·557	0·550	−0·007
40	0·926	..	0·579	0·572	−0·007
30	0·890	1·3421	0·600	0·595	−0·005
20	0·857	1·3391	0·623	0·618	−0·005
10	0·825	1·3353	0·643	0·641	−0·002
0	0·790	1·3317	0·664	0·664	0·000

There are observed in this case small but definite deviations from the additive law of magnetic susceptibility. The observed values are larger than the additive values. There seems to be also a systematic variation which reaches a maximum at concentrations between 40 and 50% of formic acid. When we have equimolecular proportions in the mixture of the acid and the alcohol, the percentage concentration of the acid in the mixture works to 59. But the maximum deviation does not occur at this concentration.

On examining the density curve shown in Fig. 3, we find that the observed values are less than the additive values. The variation in density as in the previous mixture studied is in a direction opposed to that which

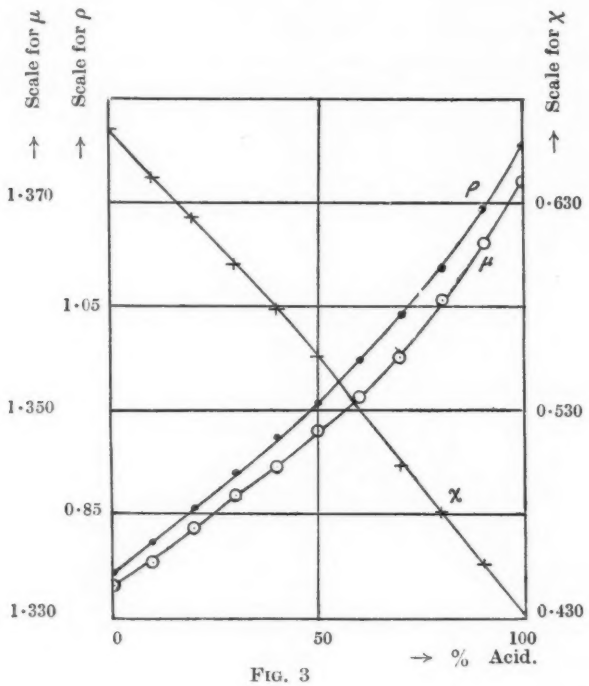

FIG. 3

is observed with magnetic susceptibility. The maximum variation of the density occurs also at about 50% concentration of the acid in the mixture. The deviation is found to be 1·6%. The refractive index curve shows a larger variation than either of the other two curves.

(*d*) *Formic Acid-Ethyl Alcohol Mixtures.*—

The results are given in Table V.

TABLE V

% of Formic acid in the mixture	ρ	μ	χ_1 observed	χ_2 calculated	$\chi_2 - \chi_1$
100	1·207	1·3722	0·433	0·433	0·000
89·7	1·135		0·461	0·464	+ 0·003
79·6	1·079	1·3680	0·493	0·494	+ 0·001
73·9	1·050	1·3667	0·514	0·511	− 0·003
69·8	1·032	1·3661	0·520	0·523	+ 0·003
66·6	1·025	1·3661	0·524	0·532	+ 0·008
59·2	0·984	1·3649	0·550	0·555	+ 0·008
54·9	0·964	1·3643	0·555	0·568	+ 0·013
49·6	0·945	1·3638	0·574	0·584	+ 0·010
38·8	0·903	1·3638	0·603	0·616	+ 0·013
30·0	0·873	1·3634	0·630	0·642	+ 0·012
20·0	0·836	1·3631	0·671	0·672	+ 0·001
10·0	0·806	1·3631	0·700	0·705	+ 0·005
0	0·781	1·3630	0·732	0·732	0·000

In this case the calculated susceptibilities are larger than the observed values. The maximum variation occurs at a concentration of 50% of the acid. At this concentration, we have equimolecular proportions of the acid and the alcohol. The maximum deviation is about 2 % of the susceptibility value at 50% concentration.

The density of the mixture also shows a deviation from the additive law. Contrary to what was observed in the previous case, we observe here the fact that the deviation of susceptibility from the additive value is in the same direction as the deviation of density.

Much stress need not be laid on the refractive index variation since in this mixture the range of variation is limited, the value for pure formic acid being 1·3722 and that for pure ethyl alcohol 1·3630. However Fig. 4 shows that the observed values of the refractive index are smaller than the additive values.

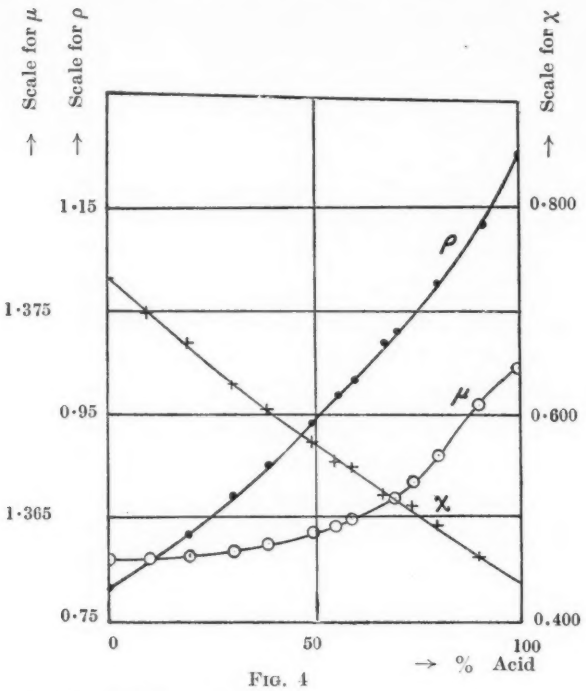

FIG. 4

(*e*) *Formic Acid-Acetone Mixtures.*—

Of the liquids investigated here, acetone has the largest electrical moment. The results are given in Table VI.

TABLE VI

% of Formic acid in the mixture	ρ	μ	χ_1 observed	χ_2 calculated	$\chi_2 - \chi_1$
100	1·207	1·3722	0·433	0·433	0·000
90	1·144	1·3701	0·438	0·447	+ 0·009
80	1·090	1·3696	0·456	0·461	+ 0·005
70	1·040	1·3684	0·478	0·475	− 0·003
60	0·994	1·3671	0·487	0·489	+ 0·002
50	0·954	1·3661	0·505	0·503	− 0·002
40	0·923	1·3655	0·514	0·516	+ 0·002
30	0·887	1·3638	0·525	0·529	+ 0·004
20	0·852	1·3616	0·543	0·544	+ 0·001
10	0·817	1·3595	0·560	0·558	− 0·002
0	0·780	1·3582	0·572	0·572	0·000

Fig. 5 presents the graph showing how these quantities vary with concentration. The refractive index varies only through a limited range and does not seem to follow the additive law. The density curve also is deviated from the straight line connecting the end points. The maximum departure occurs at about 60% concentration of formic acid and works to nearly 5% of the calculated density value assuming the additive law.

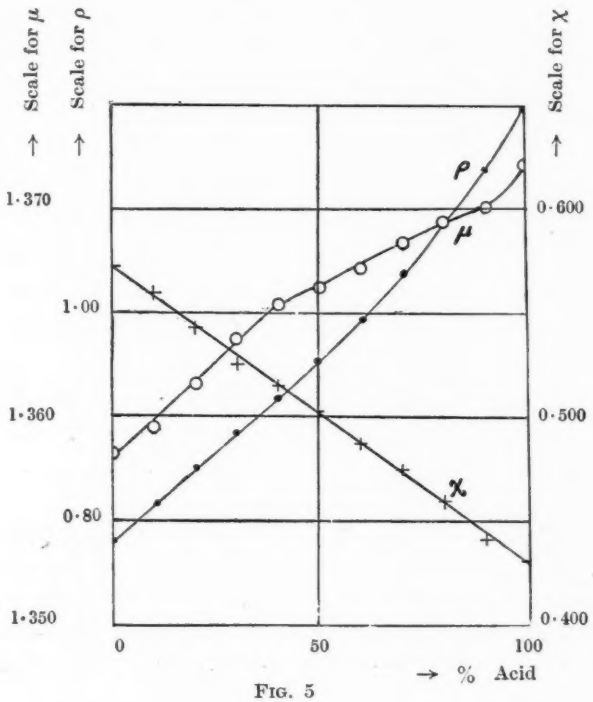

FIG. 5

The susceptibility curve shows very little deviation from the additive law. This result is also suggested by the above table. The departure is large at 90% concentration of the acid. There is no systematic variation at lower concentrations.

(*f*) *Formic Acid-Ethyl Ether Mixtures.*—

The results are tabulated in Table VII.

TABLE VII

% of Formic acid in the mixture	ρ	μ	χ_1 observed	χ_2 calculated	$\chi_2 - \chi_1$
100	1·207	1·3722	0·433	0·433	0·000
90	1·113	1·3694	0·461	0·470	+ 0·009
80	1·058	1·3682	0·490	0·495	+ 0·005
70	1·002	1·3668	0·517	0·529	+ 0·012
60	0·950	1·3650	0·555	0·561	+ 0·006
50	0·909	1·3638	0·578	0·594	+ 0·016
40	0·864	1·3612	0·612	0·626	+ 0·014
30	0·823	1·3592	0·638	0·658	+ 0·020
20	0·784	1·3578	0·675	0·698	+ 0·023
10	0·744	1·3545	0·733	0·722	− 0·011
0	0·698	1·3510	0·754	0·754	0·000

The specific susceptibility shows a definite deviation from the law of additivity. But the variation does not seem to be systematic although it looks probable that $\chi_2 - \chi_1$ increases as the percentage of ether is increased. There appears to be no connection between this variation and the concentration. The maximum variation works to nearly 3% which is a large difference.

The density curve is also deviated from the straight line connecting the end points. The refractive index curve shows a similar variation (Fig. 6).

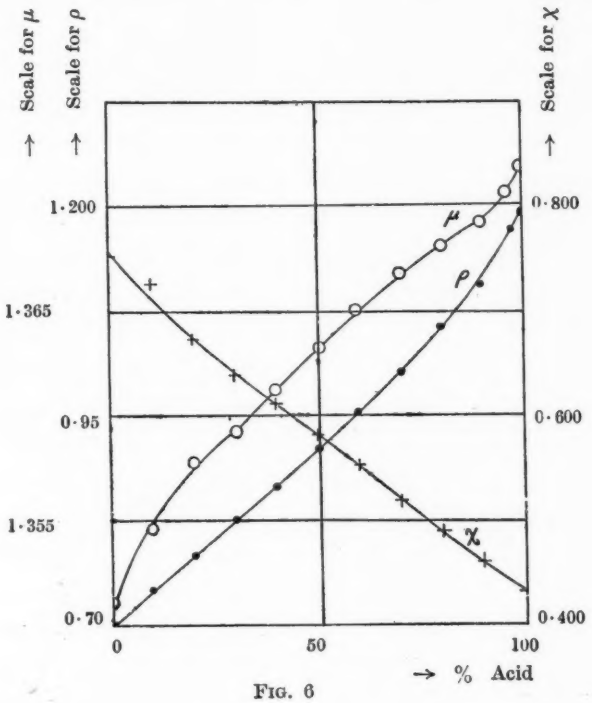

FIG. 6

(g) *Acetic Acid-Water Mixtures.*—

This mixture has been studied carefully by Rao and Varadachari. They found that the mixture obeys the additive law at different temperatures between 26° and 40° C. The results obtained here are shown in Table VIII.

TABLE VIII

% of Acetic acid in the mixture	ρ	μ	χ_1 observed	χ_2 calculated	$\chi_2 - \chi_1$
100	1·036	1·3733	0·525	0·525	0·000
93	1·048	1·3770	0·538	0·539	+ 0·001
86	1·055	1·3786	0·552	0·552	0·000
80	1·056	1·3781	0·562	0·564	− 0·002
73	1·057	1·3775	0·580	0·578	− 0·002
66	1·055	1·3750	0·593	0·591	− 0·002
60	1·052	1·3715	0·602	0·603	+ 0·001
53	1·048	1·3691	0·614	0·617	+ 0·003
46	1·043	1·3666	0·631	0·630	− 0·001
40	1·040	1·3635	0·641	0·642	+ 0·001
33	1·033	1·3590	0·655	0·656	+ 0·001
26	1·026	1·3555	0·667	0·669	+ 0·002
20	1·019	1·3516	0·679	0·681	+ 0·002
14	1·012	1·3472	0·692	0·693	+ 0·001
7	1·003	1·3440	0·705	0·706	+ 0·001
0	0·995	1·3330	0·720	0·720	0·000

On examining the table it is found that the difference is uniformly small, well within the allowable error. Thus this investigation supports the conclusions of Rao and Varadachari.[9]

The results are shown in Fig. 7. The density curve and the refractive index curve show an identical disposition. As the amount of water increases, the density and the refractive index increases at first, reach maximum values and then decrease uniformly. The maxima occur at about the same concentration, *viz.*, 75 per cent. of acetic acid.

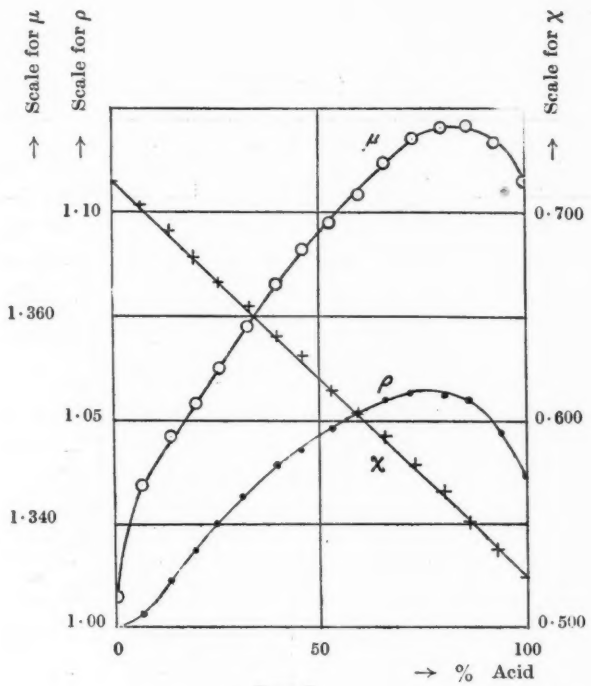

FIG. 7

(*h*) *Acetic Acid-Methyl Alcohol Mixtures.*—

The results are shown in Table IX. It will be found that at all concentrations, the observed values are larger than the calculated values. This result agrees with the conclusions obtained with formic acid-methyl alcohol mixtures. But in the present case, the exact position of the maximum if one is present at all is not clear.

TABLE IX

% of Acetic acid in the mixture	ρ	μ	χ_1 observed	χ_2 calculated	$\chi_2 - \chi_1$
100	1·036	1·3733	0·525	0·525	0·000
93·2	1·023	1·3740	0·536	0·535	− 0·001
86	1·005	1·3718	0·546	0·545	− 0·001
80	0·990	1·3690	0·555	0·553	− 0·002
74	0·975	1·3678	0·565	0·561	− 0·004
67	0·956	1·3639	0·576	0·571	− 0·005
60	0·937	1·3605	0·586	0·581	− 0·005
54	0·920	1·3571	0·592	0·589	− 0·003
46·9	0·900	1·3550	0·601	0·599	− 0·002
40	0·880	1·3513	0·612	0·608	− 0·004
33·9	0·864	1·3471	0·623	0·619	− 0·004
27	0·849	1·3440	0·630	0·627	− 0·003
19·9	0·833	1·3410	0·640	0·636	− 0·004
14·4	0·821	1·3382	0·652	0·644	− 0·008
6·8	0·803	1·3360	0·664	0·655	− 0·009
0	0·790	1·3317	0·667	0·667	0·000

The density curve in Fig. 8 lies close to the straight line connecting the end points. But the refractive index curve shows considerable variation from the additive law.

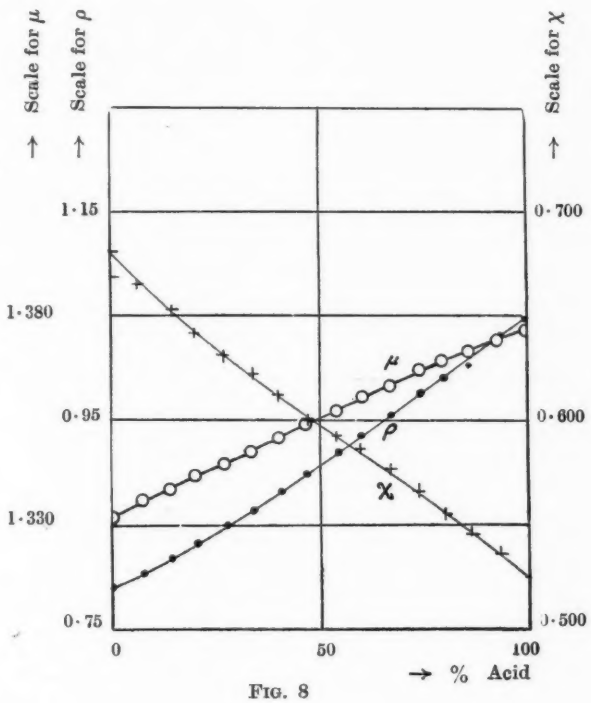

FIG. 8

(*i*) *Acetic Acid-Ethyl Alcohol Mixtures.*—

The results obtained with this mixture are tabulated below. The observed values of formic acid-ethyl alcohol mixtures were found to be less than the calculated values. In the present case a similar result is also obtained. The differences however in this case are much less than in the former mixture studied.

The density curve (Fig. 9) shows a slight departure from the additivity straight line. The maximum deviation is only 1·3 %. The refractive index curve shows much larger variation.

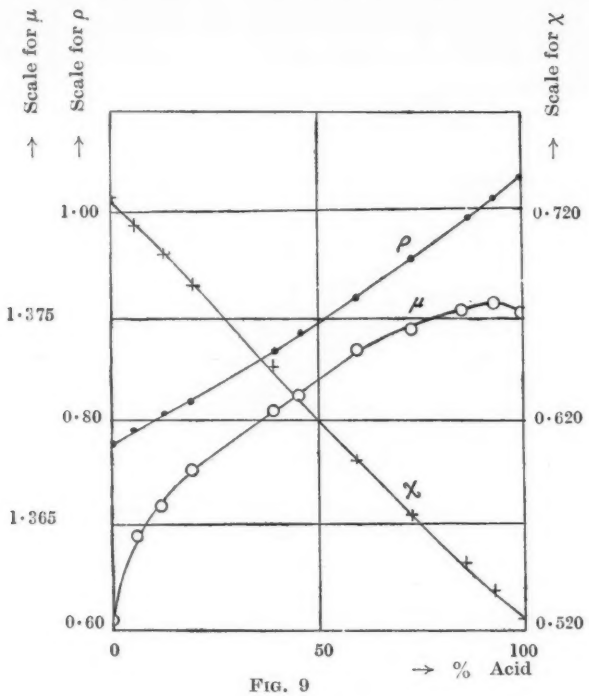

FIG. 9

TABLE X

% of Acetic acid in the mixture	ρ	μ	χ_1 observed	χ_2 calculated	$\chi_2 - \chi_1$
100	1·036	1·3733	0·525	0·525	0·000
93	1·019	1·3757	0·540	0·540	0·000
86	0·998	1·3752	0·553	0·554	+ 0·001
73	0·959	1·3744	0·575	0·580	+ 0·005
60	0·923	1·3737	0·601	0·606	+ 0·005
46	0·887	1·3714	0·634	0·635	+ 0·001
40	0·871	1·3706	0·647	0·647	0·000
20	0·822	1·3676	0·685	0·687	+ 0·002
13	0·807	1·3658	0·699	0·701	+ 0·002
6	0·793	1·3647	0·712	0·715	+ 0·003
0	0·777	1·3630	0·728	0·728	0·000

(*j*) *Acetic Acid-Acetone Mixtures.*—

The results are shown in Table XI.

TABLE XI

% of Acetic acid in the mixture	ρ	μ	χ_1 observed	χ_2 calculated	$\chi_2 - \chi_1$
100	1·036	1·3733	0·525	0·525	0·000
90	1·009	1·3738	0·536	0·530	− 0·006
80	0·982	1·3736	0·538	0·534	− 0·004
75	0·967	1·3738	0·544	0·537	− 0·007
70	0·953	1·3728	0·544	0·539	− 0·005
65	0·940	1·3730	0·548	0·542	− 0·006
60	0·931	1·3720	0·545	0·544	− 0·001
55	0·915	1·3710	0·553	0·546	− 0·007
50	0·903	1·3700	0·552	0·549	− 0·003
45	0·892	1·3692	0·554	0·551	− 0·003
40	0·878	1·3683	0·558	0·553	− 0·005
35	0·866	1·3680	0·560	0·556	− 0·004
30	0·854	1·3662	0·560	0·558	− 0·002
25	0·841	1·3650	0·563	0·560	− 0·003
16·6	0·822	1·3636	0·567	0·564	− 0·003
8·3	0·801	1·3607	0·569	0·568	− 0·001
0	0·781	1·3582	0·573	0·573	0·000

The observed values of the specific susceptibility are consistently larger than the calculated values. The density curve in Fig. 10 shows that in this case also there is a small deviation from the additive law. The refractive index values, however, show much larger deviations.

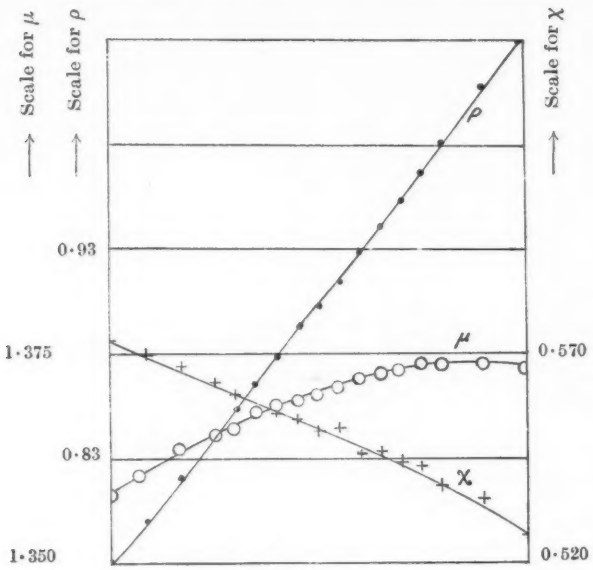

FIG. 10

(*k*) *Acetic Acid-Ethyl Ether Mixtures.*—

The results obtained are shown in Table XII.

TABLE XII

% of Acetic acid in the mixture	ρ	μ	χ_1 observed	χ_2 calculated	$\chi_2 - \chi_1$
100	1·036	1·3733	0·525	0·525	0·000
93	1·007	1·3725	0·542	0·541	− 0·001
85	0·975	1·3710	0·556	0·559	+ 0·003
77	0·945	1·3710	0·570	0·577	+ 0·007
61	0·890	1·3675	0·606	0·614	+ 0·008
54	0·867	1·3650	0·624	0·630	+ 0·006
47	0·840	1·3638	0·634	0·646	+ 0·012
40	0·820	1·3631	0·653	0·662	+ 0·009
33	0·798	1·3610	0·670	0·679	+ 0·009
27	0·781	1·3592	0·683	0·692	+ 0·009
20	0·759	1·3574	0·695	0·708	+ 0·013
14	0·742	1·3567	0·711	0·722	+ 0·011
7·5	0·722	1·3542	0·725	0·737	+ 0·012
0	0·698	1·3510	0·754	0·754	0·000

The observed susceptibility values are in this case less than the calculated values. It will be remembered that a similar deviation was observed in the case of formic acid-ethyl ether mixtures. The density values also show a small deviation, the values being less than the additivity values. The refractive index shows a much larger variation. These conclusions are obvious from an examination of Fig. 11.

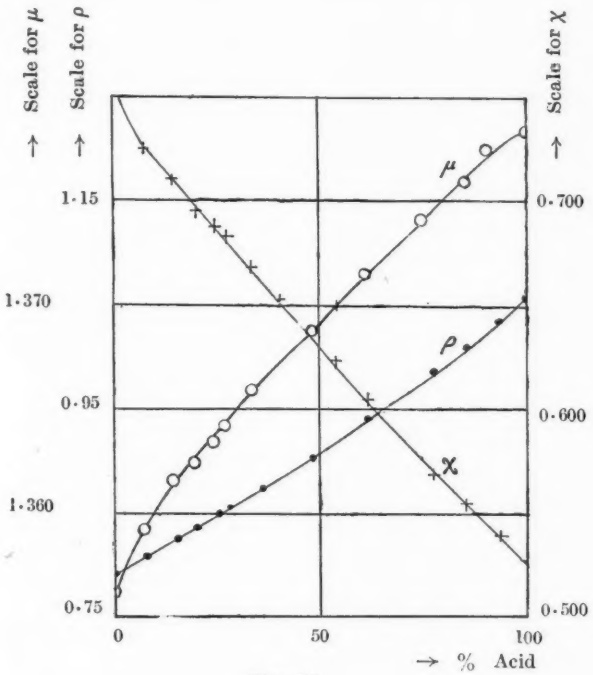

FIG. 11

(*l*) *Saturation Vapour Pressure of the Mixtures.*—

Figs. 12 and 13 give the saturation vapour pressures of the binary mixtures investigated here plotted against the concentration. The results are of great interest since the curves help us to understand the nature of the mixtures.

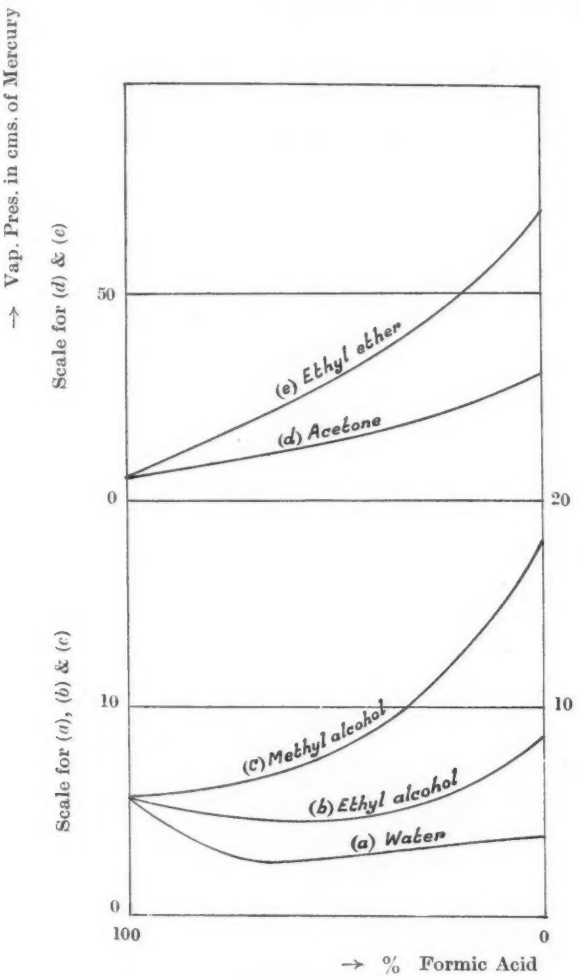

FIG. 12

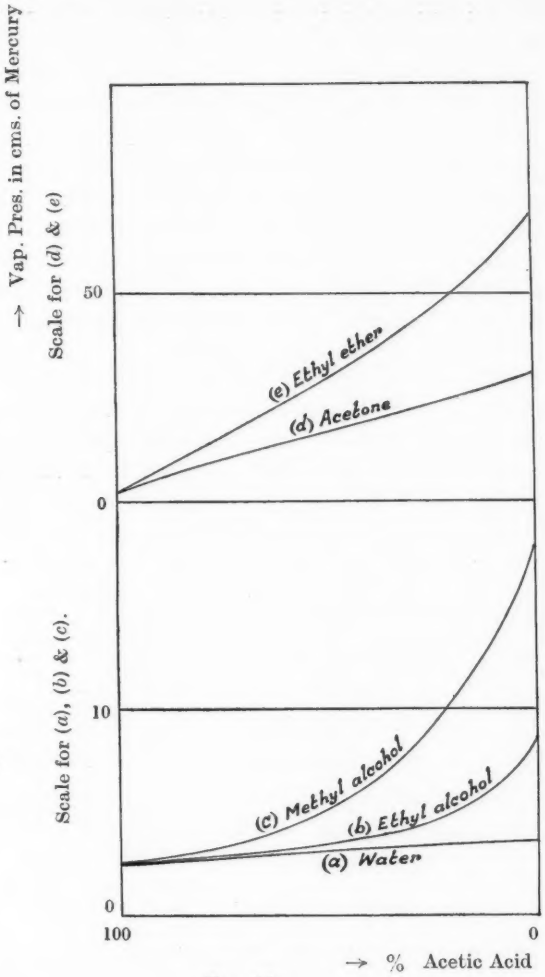

FIG. 13

Regnault investigated the pressure of the saturated vapour of mixtures of liquids. He distinguishes three cases—(*a*) When the liquids do not mix as water and benzene, the vapour pressure of the mixture is equal to the sum of the vapour pressures of the constituents. (*b*) When the liquids mix partially or dissolve each other to a limited extent, like water and ether, the vapour pressure of the mixture is less than the sum of the pressures of the constituents, or even less than that of one of them. (*c*) If the liquids mix in

all proportions the diminution of the vapour pressure of the mixture is still more marked.

We shall consider the last case. A large amount of work has been accomplished in this direction and the results indicate that there are three types of vapour pressure diagrams. When the saturation vapour pressure is plotted against composition the curve lies above or below the straigbt line joining the end points. When it lies above, there may be a sharp maximum at any concentration or there may be a gentle rise without any maximum. In all the liquids we have studied the vapour pressure curves lie below the straight lines joining the end points. The diagrams for formic acid-ethyl alcohol and formic acid-water show a distinct minimum in each case.

4. Discussion

In Table XIII the results obtained with the ten mixtures are presented. The maximum deviation obtained in each case is given as a percentage of the susceptibility value at the concentration at which the maximum deviation is noted.

TABLE XIII

No.	Mixture	Sign of $\chi_2 - \chi_1$	Maximum percentage deviation
1	Formic acid and water	+	2
2	Formic acid and methyl alcohol	−	1·3
3	Formic acid and ethyl alcohol ..	+	2·5
4	Formic acid and acetone ..		0
5	Formic acid and ether ..	+	3
6	Acetic acid and water ..		0
7	Acetic acid and methyl alcohol	−	1
8	Acetic acid and ethyl alcohol ..	+	0·8
9	Acetic acid and acetone ..	−	1·3
10	Acetic acid and ether ..	+	2

The deviations observed are obviously not due to any experimental errors or defects. The Gouy forces on each mixture were determined at four field currents (3, 4, 5 and 6 amperes) and from the susceptibilities calculated in each case, the mean susceptibility has been determined for the concentration chosen. The measurements were exactly reproducible.

The results obtained with formic acid and water support the conclusions of Rao and Sriraman. But the maximum deviation obtained by them, *viz.*, 5% is greater than the value obtained here, *viz.*, 2%. The maximum deviation however occurs at a concentration of nearly 70% in both investigations.

This observation naturally suggests the formation of the monohydrate of formic acid. Colles[22] has recorded that when a mixture of formic acid and water having the composition 4 HCOOH, 3 H_2O is cooled rapidly, crystals having 76·7 and 77·2 per cent. of formic acid are deposited. The hydrate formed in this manner at $-54°$ C. seems to be also produced at higher temperatures from a mixture of the composition 2 HCOOH, H_2O. However it is doubtful whether at the temperature of this investigation (32° C.) the monohydrate exists in such a stable manner as to effect the magnetic susceptibility.

The molecular susceptibility of formic acid is found to be 19·9. But the ionic susceptibility of the formate ion[12] is found to be only 17·3. If we assume with Kido[23] that the hydrogen attached to the formate ion in the acid does not contribute to the molar susceptibility of the acid, it is difficult to account for the higher value of the acid.

Rao and Sriraman have suggested that the higher value for the acid in the pure state is due to association of double molecules. It is more likely that the double molecules exist as a polymer. In solution, it is likely that some of the double molecules break into single molecules. Thus the observed susceptibility is lowered. The fact that the susceptibility of the formate ion is less than that of the formic acid molecule supports this explanation.

Some experimental evidence for this possibility is obtained from the work of Smyth and Rogers[24] who studied solutions of acetic acid in ether. They conclude that in solution, single and double molecules exist in equilibrium. It is likely that such a condition may also exist in aqueous solutions of formic acid.

It is of interest to observe that mixtures of formic acid and ether also give a decrease in susceptibility from the additive value. Acetic acid and ether also behave in a similar manner.

We shall next consider formic acid and methyl alcohol mixtures. There is a possibility in this case of an ester being formed.

$$HCO_2H + CH_3OH \rightleftharpoons HCO_2CH_3 + H_2O.$$

The reaction is reversible and reaches a condition of equilibrium if none of the products is allowed to escape. Formation of esters is also possible with

formic acid-ethyl alcohol, acetic acid-methyl alcohol and acetic acid-ethyl alcohol mixtures. If such a formation actually occurs, the percentage of the molecules of the acid and alcohol which interact should be very small. The change of susceptibility if any must also be small. In the following table, the molar susceptibilities of the acids and alcohols are given and their sums are compared with the sums of the molar susceptibilities of the esters formed and water. It will be seen that the susceptibility would increase in all the four cases due to the formation of esters, the increase being smallest in the case of acetic acid and ethyl alcohol. The values are for consistency all taken from Kido, whose values are close to ours.

TABLE XIV

	Acid	Alcohol	Total	Ester	Water	Total
Formic ..	19·9					
Methyl ..		22·3	*42·2*	31·1	13·0	*44·1*
Formic ..	19·9					
Ethyl ..		34·5	*54·4*	43·0	13·0	*56·0*
Acetic ..	31·6					
Methyl ..		22·3	*53·9*	43·7	13·0	*56·0*
Acetic ..	31·6					
Ethyl ..		34·5	*66·1*	53·5	13·0	*66·5*

In the present investigation, it is observed that while formic acid-methyl alcohol and acetic acid-ethyl alcohol mixtures show an increase of susceptibility, formic acid-ethyl alcohol and acetic acid-ethyl alcohol mixtures show a decrease from the additive value. Hence the entire change of susceptibility obtained in any case cannot be ascribed to ester formation.

It is thus evident that we should look to other possible methods of explanation. Seely[11] has recorded observations on nitrobenzene-carbon tetrachloride, benzene-carbon tetrachloride and nitrobenzene-benzene mixtures. Nitrobenzene which is highly polar does not show any change of susceptibility on being heated from 10° to 50° but carbon tetrachloride which is non-polar shows a temperature dependence of susceptibility. Nitrobenzene-benzene mixtures show close approximation to the principle of additivity, the departures from additivity being within the limits of precision of measurements. On the other hand, nitrobenzene-carbon tetrachloride and benzene-carbon-tetrachloride mixtures show definite departures from additivity.

It may be thus definitely established that in some organic liquid mixtures, departures from additivity exist. One possible reason that suggests itself is the effect of inter-molecular interactions which alter the energy of the least bound electrons in the molecules and bring about the change of susceptibility. The deviations observed are small and there is considerable discrepancy amongst the results of different investigators. More experimental work seems to be necessary before any detailed theory could be worked out to explain the small variations obtained.

Summary

The diamagnetic susceptibilities of binary mixtures of formic and acetic acids with water, methyl alcohol, ethyl alcohol, acetone and ethyl ether, have been investigated. The Gouy method has been adopted. The results have been corrected for the partial pressure of the air in the space above the liquid studied in the experimental tube. This has necessitated a careful determination of the saturation vapour pressure of the pure liquids and liquid mixtures. The refractive index and the relative density of these mixtures have also been studied.

The results show that considerable variations from additivity exist in the case of relative density and refractive index. The magnetic susceptibility shows the least deviation; and hence it proves to be a more nearly additive property than any other property investigated.

The deviation of the magnetic susceptibility from the additivity law does not seem to depend in any direct manner on the electrical moments of the molecules concerned. In the mixtures studied (except perhaps in the case of formic acid-water) there is little likelihood of chemical action setting in between the component liquids and producing the deviations observed. It is likely that the deviations observed are due to interaction effects between molecules. This possibility gains significance from the result of Seely, who has found that the deviations are dependent on temperatures and hence on the density of the mixture.

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ON CONTINUOUS FUNCTIONS OF A REAL VARIABLE

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Received October 26, 1938

In a recent* paper "On the Zeroes of Weierstrass' Non-differentiable Function", Dr. C. N. Srinivasiengar proves that if a knot-point of Weierstrass' function be a zero of the function, it must necessarily be a limit point of zeroes. The principle involved in this result is elucidated in Theorems VI and VII of this paper, which obtain a statement of it in a more general form.

Dr. Srinivasiengar also raises certain questions regarding the set of zeroes of Weierstrass' function, and quotes Dr. A. N. Singh's statement that 'it is desirable to find some *special* characteristic of the set of zeroes of Weierstrass' function, as for instance, whether it is closed or open, enumerable or not'. The answer to one at least of these questions is easy and well known. Namely, the set of points at which a continuous function $f(x)$ takes an assigned value a—or briefly the set S (a) of the a-points of $f(x)$—is necessarily a closed set. I concern myself here with these questions, in so far as they relate to the *general* continuous function.

I. The Closed Sets Associated with a Continuous Function

Let $f(x)$ be a continuous function defined in a closed internal (0, 1) say. Let L and U be the lower and upper bounds of $f(x)$; and let a be any number such that $L \leqslant a \leqslant U$. Then the set S (a) of solutions of the equation

$$f(x) = a$$

is not empty, in virtue of the continuity of $f(x)$.

Theorem I. *S (a) is a closed set.*

This is an immediate consequence of the definition of continuity; namely, $f(x)$ is continuous if $\lim_{y \to x} f(y)$ exists and is equal to $f(x)$.

We now make the assumption that the set of points of non-differentiability of $f(x)$ is everywhere dense in the interval (0, 1); this includes the case

* *Journal of the Indian Mathematical Society*, Sep. 1938.

in which $f(x)$ is non-differentiable throughout the interval. With this assumption, we have

THEOREM II. *$S(\alpha)$ is closed and non-dense.*

For, if $S(\alpha)$ contains any subinterval of the interval $(0, 1)$, then $f(x)$ would be equal to α throughout the subinterval, and hence be differentiable in it. This contradicts the hypothesis that the set of points of non-differentiability of $f(x)$ is everywhere dense. Hence $S(\alpha)$ cannot contain any sub-interval and is therefore non-dense.

By a classical theorem in the theory of sets of points, a closed non-dense set can be decomposed into an enumerable set, and a perfect (non-dense) set. Since a perfect set has the cardinal number of the continuum, it follows that $S(\alpha)$ will be enumerable if it has no perfect component, and will have the cardinal number of the continuum if it has. The following considerations shew that no better result than this can be stated for the general continuous function :

(1) Given any enumerable set E in $(0, 1)$, it is not difficult to shew that we can construct a continuous function, which vanishes (or takes an assigned value α) at all points of the set E and at no other points.

(2) Given any perfect (non-dense) set, it is shewn below under Theorem III how we can construct a continuous function which vanishes at all points of the set.

(3) Even for special values of α—say $\alpha = L$ or U—no better result can be stated. A proof that the *proper* maxima and minima of a continuous function form an enumerable set will be found in Hobson's *Functions of a Real Variable*. But this by no means implies that the set $S(L)$ or $S(U)$ is enumerable.

THEOREM III. *The set $S(\alpha)$ is of measure zero, except possibly for an enumerable set of values of α in (L, U).*

Proof.—Since $f(x)$ is continuous, the set $S(\alpha)$ is measurable. From the property of measurable sets, it follows that the sum of the measures of the sets $S(\alpha)$ for any sequence of values of α must be equal to or less than 1 [which is the measure of the whole interval $(0, 1)$]. Hence if ϵ is any positive quantity, the measure of $S(\alpha)$ can be greater than ϵ only for a finite number of values of α. Hence it follows at once that the set of values of α for which $S(\alpha)$ has a measure greater than zero, must be enumerable.

To see that Theorem III is a best possible result even if $f(x)$ is non-differentiable, we may shew how to construct a continuous function which

vanishes at all points of an assigned perfect set (irrespective of whether the perfect set has a measure equal to or greater than zero), and is non-differentiable.

To construct a perfect non-dense set, we start with a sequence $n_1, n_2, \cdots$ of positive numbers greater than 1. We remove symmetrically from the middle of the interval (0, 1) a subinterval of length $\frac{1}{n_1}$, ; we then remove symmetrically from the middle of each of the two intervals left, a fraction $\frac{1}{n_2}$ and so on *ad infinitum*. What remains after the sequence of removals is the set of endpoints of the intervals removed, and the limit points of these endpoints. These constitute a perfect non-dense set of measure θ given by :

$$\theta = \left(1 - \frac{1}{n_1}\right)\left(1 - \frac{1}{n_2}\right)\left(1 - \frac{1}{n_3}\right)\cdots.$$

We can obviously choose the sequence $(n_1, n_2 \cdots)$ so that θ is zero or any positive number less than 1.

We now define a continuous function $f(x)$ as follows. We define $f(x) = 0$ if x is any point of the perfect set thus constructed. If x is not a point of the perfect set, it is an interior point of a definite one of the intervals removed—say, the nth interval $(\alpha_n \beta_n)$. We then define $f(x)$ by :

$$f(x) = \sum_{m=0}^{\infty} a^m \sin b^m \pi \cdot \frac{x - \alpha_n}{\beta_n - \alpha_n} \cdot \left(ab > 1 + \frac{3\pi}{2}\right) (\alpha_n < x < \beta_n),$$

so that within each of the intervals removed, $f(x)$ is a Weierstrassian non-differentiable function, vanishing at the endpoints of the interval. The function $f(x)$ thus defined by an enumerable set of specifications in (0, 1) is continuous and non-differentiable and vanishes at points of the perfect set of measure θ.

II. The Derivatives of a Continuous Function

I shall next proceed to study the relation of the sets S (α) to the concept of 'derivate,' which is really the subject-matter of Dr. Srinivasiengar's result. The treatment of the notion of 'derivate' which I give here seems to be an improvement on the treatment to be found, *e.g.*, in Hobson *l.c.*

THEOREM IV. *If* ϕ (h) *is* any *function whatever, defined in the open interval* (0, k), *the set of limits of* ϕ (h) *as* $h \to +0$ *is a closed set.*

A proof of this will be found in Hobson (*loc. cit.*) As a matter of fact, no special proof is called for, as the theorem is only a particular statement of the fact that the derived set of any set whatever is a closed set.

THEOREM V. *If the* ϕ (h) *of Theorem IV is continuous in the open interval* $(0, k)$, *the closed set of limits of* ϕ (h) *as* $h \to 0$ *is a closed interval.**

To prove this, let ϕ_1, ϕ_2 be any two functional limits of ϕ (h) as $h \to +0$, and let the corresponding sequences of values of h be $(h_1, h_2, \cdots)$, $(h_1', h_2', \cdots)$, so that :

$$\operatorname*{Lim}_{n \to \infty} h_n = \operatorname*{Lim}_{n \to \infty} h_n' = +0 \; ; \; \phi_1 = \operatorname*{Lim}_{n \to \infty} \phi \; (h_n) \; ; \; \phi_2 = \operatorname*{Lim}_{n \to \infty} \phi \; (h_n').$$

Let $\phi = t\,\phi_1 + (1-t)\,\phi_2$ $(0 < t < 1)$ be any number between ϕ_1, ϕ_2. To prove that ϕ is also a limit of ϕ (h), we observe that $t\,\phi\,(h_n) + (1-t)\,\phi\,(h_n')$ is a number between the two values ϕ (h_n), ϕ (h_n') of the continuous function ϕ and is therefore a value of ϕ at some point H_n of the interval (h_n, h_n'). It is clear that as $n \to \infty$ $H_n \to 0$, and $\operatorname{Lim} \phi\,(H_n) = \phi$. This proves that when ϕ is continuous, the closed set of functional limits of ϕ (h) is a closed interval.

THEOREM VI. *If in Theorem V,* t *is an interior point of the closed interval of functional limits of* ϕ (h), *we can find two sequences* (h_n), (h_n') *tending to* $+0$, *such that* $[\phi\,(h_n)]$ *tends to* $(t + 0)$, *and* $\phi\,(h_n')$ *tends to* $(t - 0)$.

If t *is an endpoint of the interval of functional limits, it may or may not be possible to find two sequences* (h_n), (h_n') *with this property.*

The theorem will be proved, if we can shew that are values of ϕ (h) in each of the intervals $(t, t \pm \epsilon)$ for every positive ϵ. Since $t \pm \frac{\epsilon}{2^m}$ $(m = 1, 2, \cdots)$ are all limits of ϕ (h), we can find h_n, h_n' so that

$$\left.\begin{aligned} \left|\phi\,(h_n) - \left(t + \frac{\epsilon}{2^n}\right)\right| &< \frac{\epsilon}{2^{n+1}} \\ \left|\phi\,(h_n') - \left(t - \frac{\epsilon}{2^n}\right)\right| &< \frac{\epsilon}{2^{n+1}} \end{aligned}\right\} \; n = 1, 2, \cdots$$

The sequences $\phi\,(h_n)$, $\phi\,(h_n')$ tend to t from different sides as $n \to \infty$, so that the first part of the theorem is proved.

This proof is no longer valid if t is an endpoint of the interval of functional limits. But it is easy to construct examples which shew that t may still be approachable as a functional limit from both sides.

We now apply theorems V and VI to the function ϕ (h) which is equal to the incrementary ratio $\dfrac{f\,(x+h) - f\,(x)}{h}$ of the continuous function $f\,(x)$ at the point x. This function ϕ (h) is continuous in open intervals on either

* For theorems of this sort in Anaysis, it is convenient to consider the real number continuum as a closed interval with the endpoints $+\infty$ and $-\infty$.

side of the endpoint $h = 0$. By Theorem V, the functional limits of $\phi(h)$ as $h \to +0$ and -0, constitute respectively two closed intervals. I shall call these intervals the *right* and *left derivate-intervals* of the continuous function $f(x)$ at the point x.

Suppose now that $f(x) = \alpha$, so that x belongs to the closed set S (α). If a right neighbourhood $(x, x + h)$ of x can be found, throughout which $f(x) > \alpha$ $(< \alpha)$, we say that $f(x)$ is *increasing* (*decreasing*) on the right of x. If in every small right neighbourhood $(x, x + h)$ $f(x) \geqslant \alpha$ $(\leqslant \alpha)$, we say that $f(x)$ is *non-decreasing* (*non-increasing*) on the right of x. If in every small right neighbourhood $(x, x + h)$ of x there are points at which $f(x) > \alpha$ as well as points at which $f(x) < \alpha$, we say that $f(x)$ is *oscillatory* on the right of x.

It is obvious that if 0 be external to the right derivate interval of $f(x)$ at x, then $f(x)$ must be either increasing or decreasing to the right of x. If however 0 is an endpoint of the right derivate-interval, all possibilities are open for the behaviour of $f(x)$ on the right of x.

If x is a *limitpoint* of the set S (α), approached say from the right, it is clear that 0 must belong to the right derivate-interval. Is the converse of this theorem true? Theorem VI shows that the converse can be asserted categorically, only if it is known that 0 is an *interior* point of the derivate-interval.

THEOREM VII. *If* 0 *is an interior point of the right derivate-interval of* f (x) *at* x, *then* f (x) *is necessarily oscillatory on the right of* x. *Also* x *is necessarily a limitpoint of* S (α) *approached from the right, where* $\alpha =$ f (x).

Since, by hypothesis, 0 is an interior point of the derivate-interval, it follows from Theorem VI, that the incrementary ratio can approach zero from either side as $h \to +0$. Hence $f(x)$ must be oscillatory to the right of x. Hence in every right neighbourhood of x, there are points at which $f(x) > \alpha$, as well as points at which $f(x) < \alpha$. Hence, since f is continuous, there are in every right neighbourhood of x, points at which $f(x) = \alpha$; in other words x is a limitpoint of S (α) approached from the right.

The point x is said to be a *knot-point* of $f(x)$, if both the derivate-intervals at x extend from $-\infty$ to $+\infty$. In such a case zero is an interior point of both the derivate-intervals. Hence a knot-point x of f is necessarily a limitpoint on both sides of the set S (α) $[\alpha = f(x)]$—which is Dr. Srinivasiengar's result.

It is clear that a result corresponding to Theorem VII can be stated for any other value of the derivate.

CHEMICAL EXAMINATION OF THE ESSENTIAL OIL OF *OCIMUM SANCTUM* LINN.

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Received October 19, 1938

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

Ocimum Sanctum Linn. or *Tulsi* as it is known in Bengali and Hindi is a strongly scented low shrub with erect stems belonging to the natural order of *Labiatæ*. When carefully cultivated, *Tulsi* plants have been known to grow to a height of nearly five feet and the lower stems become quite woody under such circumstances. Throughout India, the plant is regarded as sacred amongst the Hindus and in all religious affairs and devotional worships, the leaves of *Tulsi* are essential and used as offerings to deities along with flowers and Bel (*Aegle marmelos*) leaves. In almost every Hindu household, at least one Tulsi plant is grown for this purpose, and in many parts of the country the plant is held in such veneration and devout esteem that it is actually worshipped as a deity.

The leaves of *Tulsi* have very interesting medicinal properties, for which purpose also they are almost indispensable in every household. The juice of the leaves have strong expectorant properties, and on account of this, is used in catarrah, cough, bronchitis and other ailments of the respiratory system. A thick paste of the leaves ground up with water is used in various cutaneous affections, like ringworm, itch, scabies, eczema, etc. An infusion of the leaves is very beneficial in digestive disturbances of the children and in hepatic affections. The leaves have been successfully employed in many cases of jaundice and liver disorders. According to Kirtikar and Basu,[1] the dried and powdered leaves are employed as snuff in ozœna. The leaves have very strong antisepetic and disinfectant properties. Cuts, burns, bruises and sores when treated with a paste of the leaves, heal very quickly without becoming septic. The juice of *Tulsi* leaves is also supposed to be a specific against earache, and a decoction of the leaves is efficacious in disorders of the genito-urinary system. Woollen and silk clothes and also furs when kept in closed vessels interspaced with *Tulsi* leaves, are not at all attacked by destructive insect pests which are such a terrible nuisance in India during the hot months of the year. The leaves of the *Tulsi* plant are also reputed to have the property of warding off the mosquito.

A full description of the *Tulsi* plant has been given by Roxburg,[2] and so it is omitted here. Two photographs of the plant are however appended.

The essential oil of *Tulsi* which is presumably responsible for all the medicinal properties of the plant, is very easily removed from the leaves in which it is mainly present, by distillation with steam, and from the distillate, the oil can be extracted with petroleum ether. The proportion of essential oil in the leaf varies according to the kind and quality of the plant and the mode of its cultivation, but the average of a large number of experiments has come to about 0·7 per cent. The dark variety of *Tulsi* contains more essential oil than the lighter variety.

The crude essential oil of *Tulsi* gives a deep bluish green coloration with alcoholic ferric chloride and is strongly phenolic in nature. It was resolved by aqueous sodium hydroxide into phenolic and non-phenolic constituents. The phenolic portion on distillation and rectification was resolved into a very small fraction consisting of carvacrol and a large fraction consisting of eugenol. The non-phenolic portion on similar treatment was resolved into a main fraction consisting of eugenol methyl ether. The constituents were identified by preparation of suitable derivatives and also by direct comparison with authentic specimens. In addition to eugenol methyl ether, the non-phenolic portion contained a high boiling terpene hydrocarbon which appeared to be caryophyllene from qualitative reactions, but it could not be definitely identified for want of sufficient material.

In this connection it is rather interesting to note that both eugenol and eugenol methyl ether have been found together in *Cinnamomum pedatinerium* of Fiji by Goulding[3] and also in the oil of *Asarum canadense* by Power and Lees.[4] Eugenol together with its methyl ether has also been found in the essential oils of Acacia, Bay, Culilaban, Laurel, Pimento and Massory according to the report of Allen.[5]

Experimental

Essential Oil of Tulsi.—For the preparation of the essential oil of *Tulsi*, the fresh leaves in lots of three kilos each time were distilled with water from a large distilling apparatus made of copper and fitted with a copper worm condenser, until the distillate which was opalescent in the beginning began to run perfectly clear. The distillate (5 litres) was shaken with petroleum ether in a large separator, and the upper petroleum ether layer after dehydration with anhydrous sodium sulphate was distilled from a water-bath until the petroleum ether no longer came over.

The crude essential oil of *Tulsi* thus obtained is a clear bright yellow oil with a characteristic odour of the plant admixed with a strong note of cloves. With alcoholic ferric chloride, the substance gives an intense greenish blue coloration. It reduces ammoniacal silver nitrate, but not Fehling's solution. It is soluble in an aqueous solution of sodium and potassium hydroxide to the extent of over 70 per cent. by volume. This method of treatment was therefore utilised in the separation of the phenolic and non-phenolic constituents of the oil.

Separation of the phenolic and non-phenolic constituents of the essential oil of Tulsi.—The crude oil (100 c.c.) was taken in a separating funnel and diluted with an equal volume of petroleum ether. Aqueous caustic soda (5 per cent. 100 c.c.) was added and the mixture vigorously shaken. On allowing to stand for a short time, two layers separated out, and the lower dark red aqueous layer was removed Two more extractions of the upper petroleum ether layer with aqueous caustic soda were done in the same way as before, using half the previous volume of alkali each time. The combined alkaline extract was acidified with concentrated hydrochloric acid, and the separated dark red oil taken up with petroleum ether. After dehydration with anhydrous sodium sulphate, the petroleum ether was distilled off from a water-bath when the phenolic constituent of the essential oil of *Tulsi* was left behind as a dark red heavy oil (A) with an intense smell of cloves

The non-phenolic constituent of the essential oil of *Tulsi* left behind in the petroleum ether layer in the above extraction process, was freed from petroleum ether on the water-bath and was obtained as a bright yellow oil having a characteristic odour resembling that of the leaves of the plant (B).

Rectification of the Phenolic Constituent (*A*)

This was done by fractional distillation under ordinary pressure, using a distilling flask of about 150 c.c. capacity with a rectifying neck of four bulbs blown below the delivery tube. The following fractions were collected, the mercury thread of the thermometer shooting up in between the different ranges of temperatures indicated :

TABLE I

Total quantity taken = 77 *c.c.*

Fraction No.	Boiling range °C.	Quantity of distillate in c.c.
1	upto 130	10·0
2	232–236	3·0
3	245–248	62·0
4	255–260	1·5
5 (residue)	..	0·5
	TOTAL ..	77·0

Fraction No. 1 was the higher boiling fraction of petroleum ether and was quite colourless and chemically non-reactive.

Fraction No. 2 was a pale yellow oil with a characteristic odour of thyme or horse mint, and gave an intense green coloration with alcoholic ferric chloride. It yielded a liquid acetyl and a benzoyl derivative. The substance was identified to be *carvacrol.*

Fraction No. 3 was a pale yellow thick and heavy oil with an intense smell of cloves. It had a specific gravity of 1·069 at 25° C., and gave a blue coloration with alcoholic ferric chloride. It reduced ammoniacal silver nitrate, but not Fehling's solution. The benzoyl derivative prepared by the action of benzoyl chloride on the substance dissolved in excess of 5 per cent. solution of sodium hydroxide, on recrystallisation from dilute alcohol, melted sharp at 69° C. and the melting point was not depressed on admixture with an authentic specimen of benzoyl-eugenol, specially prepared for this purpose from Merck's pure eugenol.

Fraction No. 4 was a yellow thick oil, but lighter than water. On account of the small quantity available, it could not be definitely identified, but as far as it could be seen from qualitative reactions, it appeared to be a terpene ketone or phenol of complex composition.

Rectification of the Non-phenolic Constituent (B)

This was also done by fractional distillation under ordinary pressure exactly in the same way as the phenolic constituent (A). The results are summarised in Table II :

TABLE II

Total Quantity taken = 24 *c.c.*

Fraction No.	Boiling range °C.	Quantity of distillate in c.c.
1	upto 130	4·0
2	246–249	18·0
3	258–265	1·4
4 (residue)	..	0·6
	TOTAL ..	24·0

Fraction No. 1 was only the higher boiling fraction of petroleum ether used in the extraction of the oil.

Fraction No. 2 was a pale yellow oil, which on redistillation boiled completely between 248–249° C. It had a peculiar characteristic odour resembling to a great extent the odour of the leaf, with a strong note of betal-leaf. It had all the properties of *eugenol methyl ether*, and on oxidation with alkaline potassium permanganate, yielded veratric acid melting at 179° C. The melting point of the veratric acid obtained in this way did not get depressed on admixture with an authentic specimen of veratric acid obtained from Messrs. Schuchardt.

Fraction No. 3 was a yellow oil, lighter than water, and with a characteristic resinous smell. The quantity obtained was too insufficient for carrying out any systematic tests, but from qualitative reactions, it appeared to be *caryophyllene*.

Summary and Conclusions

1. The essential oil of *Ocimum Sanctum* Linn. or *Tulsi*, is a pale yellow oil obtained from the leaves of the plant in an yield of 0·7 per cent. by steam distillation.

Ocimum Sanctum Linn. View of entire plant

Ocimum Sanctum Linn. Near view of the leaves and branches

2. The oil has the characteristic odour of the leaves together with a strong note of cloves and is strongly phenolic in nature.

3. The oil was resolved into phenolic and non-phenolic constituents by aqueous sodium hydroxide, and from the phenolic portion, carvacrol and eugenol were definitely isolated and identified. From the non-phenolic portion, eugenol methyl ether was definitely identified, and the presence of caryophyllene was tentatively shown.

4. The essential oil of *Tulsi* contains over 71 per cent. of eugenol and 20 per cent. of eugenol methyl ether together with about 3 per cent. of carvacrol. As it is, the oil is an excellent source of eugenol which is used in the preparation of vanillin.

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A PHOTOELECTRIC NEPHELOMETER FOR CHEMICAL ANALYSIS

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Received November 22, 1938

Introduction

Chemical analysis of substances by measurement of the amount of light (i) absorbed, in case of dissolved substances and (ii) reflected, in case of suspended ones, has assumed considerable importance in analytic procedures in recent years. In a previous communication[2] from these laboratories the authors described a new instrument for chemical analytic purposes by measurement of the absorbed light. The present contribution deals with a physical instrument and an outline of the procedure for the analysis of suspended substances by measurement of the reflected light.

The chief advantages of the nephelometers, *i.e.*, instruments for chemical analysis of suspended substances by measurement of reflected light, are their convenience of operation, the large number of analyses that can be done at a time and the possibility of measuring with their aid concentrations which are measurable only with great difficulty, if at all, by gravimetric methods. However, the nephelometers do suffer from certain inherent limitations which need elimination. The dependence on the ability of the eye in the matching of light introduces a personal error in the estimations. Moreover, colour blindness, a defect not uncommonly met, dispenses with the use of the visual nephelometers. The two types (i) "constant upper end type" and (2) "constant lower end type" to which the nephelometers conform, differ in the distance that the light from the longer of the two illuminated and measured columns has to travel from the particles to the eye-piece—greater and smaller (respectively) than that from the shorter column. This variation in the distance factor, must necessarily introduce a certain amount of inaccuracy. Further, any arrangement, dispensing with the use of the plunger, which is likely to disturb the size or dispersion of the suspended particles, is desirable.

The frequent necessity of making a large number of quantitative estimations of soil and plant constituents, by the production of insoluble precipitates, has repeatedly called for simplifying the procedure so as to eliminate

the possibilities of personal error in observations, to detect more minute differences than is possible by the preceding methods and to be applicable for varied purposes. The new instrument described here circumvents some of the defects of the visual nephelometer and allows of certain additional advantages.

Principle

A turbid fluid possesses the property of causing a part of the light illuminating it to be deviated from its original direction and be diffused. The brightness of the light reflected, *i.e.*, opacity, is due to small particles in suspension in the liquid. The intensity of light reflected depends upon (i) the number of particles in suspension and (ii) their size.[3] Provided the latter is kept constant, *viz.*, by the production of suspension with uniform sized particles and comparison with an invariable standard of turbidity the intensity of the light scattered in a certain direction affords a measure of the amount of the suspended particles.

The method described here essentially consists in measuring the intensity of scattered light coming from an illuminated column of suspended substance* with the light scattered from an invariable standard of turbidity, *viz.*, frosted glass discs, with the aid of a quantitatively variable light diminution. With a view to obtaining precision in measurements, and to correct for the differences in tint in the light reflected by the suspension and standard, the measurements are made within the range of any one of the appropriately selected colour filters blue (450–510 $\mu\mu$), green (520–560 $\mu\mu$), and red (620–680 $\mu\mu$).

From a calibration graph where the turbidity values are plotted against a series of known concentrations any observational reading may then be read off directly.

Apparatus

The essential features of the apparatus may readily be seen from the schematic diagrams (Figs. 1 and 2).

The source of light L is a 30 watt 8 volt " Nitra " lamp supplying an intense light which is regular and easily adjustable. Two equal beams of light from the lamp enter through the two lenses A_1 and A_2, the chambers C_1 and C_2 containing the turbid solution and the comparison standard respectively, in the form of a parallel pencil of rays square in section. The lights scattered by the suspended particles in the turbid liquid, and by the frosted

* The reaction producing the suspension should result in particles of uniform size and stability.

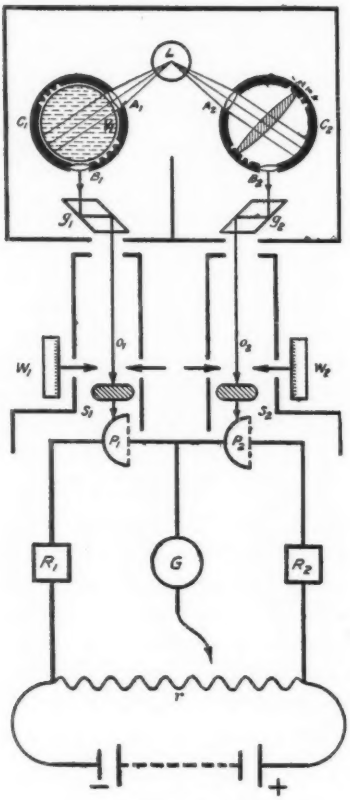

FIG. 1

Schematic diagram of Photoelectric Nephelometer
The Vessel V_2 is not shown in the figure

glass disc (standard) pass through the lenses B_1 and B_2 and the prisms I_1 and I_2 into the two measurably variable light apertures O_1 and O_2 (Fig. 2—to be described further) at an angle of 45° to the incidence. The light rays from the two apertures pass through S_1 and S_2, the slots for the reception of the colour filters within the range of which a particular measurement has to be made. The lights from S_1 and S_2 then activate the photoelectric cells* P_1 and P_2 respectively. The cells are continuously in circuit, the latter being of the bridge type employed by the authors in their previous instrument.[2] R_1 and R_2 are the protective resistances of 10,000 ohms each, r_1 a variable

* Cæsium cells (Becker & Co.).

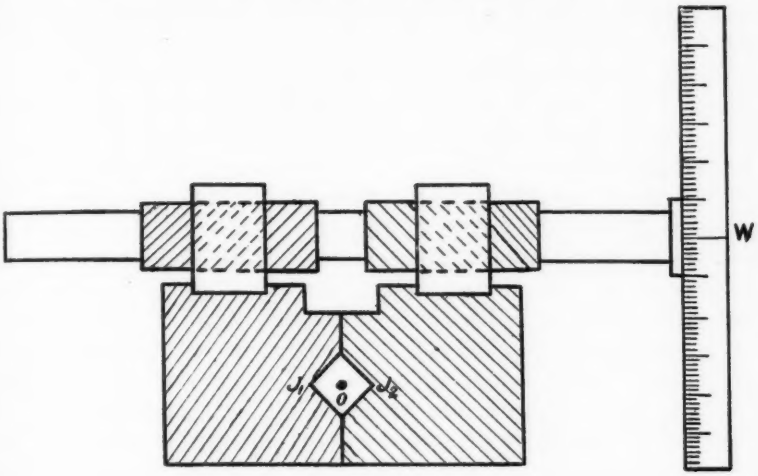

FIG. 2

FIG. 2. Variable light diaphragm of Photoelectric Nephelometer

resistance and G, the galvanometer with a sensitivity of 0·025 micro-amperes per mm. scale reading.

Standard for comparison.—The light used as a basis for comparison with the turbid medium passes through one of the four frosted glass discs of varying opacity (refer Fig. I, –1, 2, 3, 4). Each of these four discs is standardised by comparison with a body of translucent* glass which is for all practical purposes invariable.

Compensating mechanism.—The light measuring device is a compensating mechanism of the nature of a variable light diaphragm (Fig. 2). Each of the apertures O_1 and O_2 (Figs. 1 and 2) can be measurably varied by means of the two V-shaped jaws j_1 and j_2 in such a way that the centre of the aperture always coincides with the optic axis. The ratio of the two amounts of light entering is proportional to the ratio of the areas of the two apertures. The scale readings† etched on the recorder W give a measure of the reflected

* Supplied by Carl Zeiss Zena: Standardisation is effected by ascertaining the fraction of light which is dispersed in the opaque glass at an angle of 45° to the direction of illumination.

† If i = intensity of the reflected light (equals the area of the aperture), d = the variable diagonal between 0 and D of the square aperture and α = angle between 0 and 360° through which W turns then,

(i) $i = (d/\sqrt{2})^2 = (\alpha\ 360)^2$ for d from 0 to D and α from 0° to 360° and,

(ii) $\alpha = i \cdot 360° = 0$ up to 360° for i from 0 to 1.

light as a percentage of the incident, 100 being the largest opening and 0 the smallest.

Operation.—The turbid fluid under examination is put into two convenient containers V_1 and V_2 (see below), and the latter inserted in chambers C_1 and C_2 and the light turned on. If the instrument is optically and electrically symmetrical, the galavanometer should show no deflection. But in practice this is not attained as slight differences in the arrangement are unavoidable and also on account of slight variation in the response of the photocells as no two photocells are identical. These slight variations are eliminated by the use of the common battery shunted by *r*. Hence using *r* as a fine adjustment the null-point is obtained. After this preliminary adjustment the light is switched out. The container with the turbid liquid is removed from chamber 2 (C_2, Fig. 1) and the light switched on again. Now on account of the difference in the intensities of the lights falling on the photocells the bridge is thrown out of balance and is indicated by the deflexion of the galvanometer (G). An appropriate frosted glass disc is then introduced* into the respective slot of the chamber C_2 such that the two intensities are approximately equal as indicated by the least deflexion of the galvanometer. The final compensation† is then effected by turning the appropriate recorder (left if turbid solution is brighter than standard and right if *vice versa*) till the null-point on the galvanometer is restored.

The measurement is repeated interchanging the positions of the turbid fluid and the frosted glass disc and the average of the two readings taken.

Calculations.—If *o* be the scale reading, *t* the opacity of the standard, *d* the value of the size of the vessel, S the correction factor for filter used (taking blue as standard) then opacity T of the turbid fluid is given by $T = (o.d.t.)\,S$.

Having obtained the value for opacity the concentration is read off from a calibration graph.

Accuracy.—A factor which greatly influences the accuracy of the determinations is the size of the vessel. Fig. 3 indicates the relationship between turbidity and concentration with different vessels. Needless to say that measurement with any particular vessel should be made in the region of linear proportionality, which nevertheless is of considerable extent.

The possibility of an imperfect return of the photocells to their original current output after having been exposed to the irregularities of light intensity associated with experimental procedures is likely to introduce errors.

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* All four to be tried successively.

† The difference in the intensity of scattered light between the suspension and standard should be within a ratio 1 to 3. Otherwise, inaccuracies are encountered. In practice, this difference is not generally exceeded.

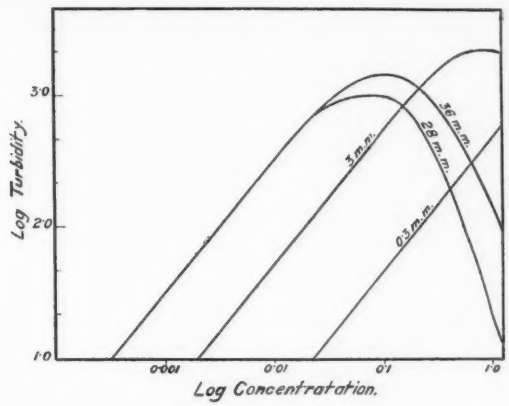

FIG. 3

Relationship between turbidity and concentration with different vessels

These can however be overcome by the selection of the proper filter, appropriate readjustment of the instrument and checking its readings at expedient intervals.

The reagent used should produce suspensions of equal dispersive power (equal sized particles) and also the suspensions produced should be fairly stable. This necessitates a preliminary testing of the possible precipitants and " protective colloids " for each substance, before successfully employing the apparatus.

The accuracy of the apparatus was tested by estimations of phosphorus following the method perfected by Kober and Egerer[1] for the production of a colourless, uniform and stable suspension. The method depends upon the production of a nephelometric cloud with the strychnine-molybdic acid reagent in HCl. The turbidity is proportional to the phosphorus content. The data are given in Table I.

A glance at the table shows that an accuracy of $\pm$ 2·4 per cent. is easily obtained in practice.

For the estimation of phosphorus in plant sap, 10 c.c. of the sap is digested with 20 c.c. of H_2SO_4 (sp. gr. 1·84) and 8–9 gm. of K_2SO_4 until a clear solution is obtained. Then the melt is cooled, dissolved in water and made up to 500 c.c. 25 c.c. of the solution are pipetted out, neutralized with NH_4OH, filtered through a dry, acid-washed filter paper, and the filtrate diluted to 200 c.c. 10 c.c. of this diluted solution are treated with the reagent, as given above and the suspension estimated after 4-6 minutes standing. On reference to a previously calibrated graph, the concentration corresponding to the observational reading is obtained.

TABLE I

Determination of phosphorus with the Photoelectric Nephelometer

To 100 c.c. of potassium phosphate solution of the indicated concentration are added 30 c.c. of distilled water, 5 c.c. of 0·5 NHCl and 5 c.c. of strychnine-molybdic acid reagent

Phosphorus present	Phosphorus found	Deviation	Error*
mg. per 100 c.c.	mg. per 100 c.c.		..
0·013	0·0132	+ 0·0002	1·6
0·016	0·0164	+ 0·0004	2·13
0·022	0·0215	− 0·0005	2·30
0·034	0·0334	+ 0·0004	1·7
0·041	0·0418	+ 0·0008	1·96
0·062	0·0612	− 0·0009	1·40
0·082	0·0811	− 0·0009	1·25
0·084	0·0820	− 0·002	2·4
0·090	0·0910	+ 0·001	1·2

* Each an average of 10 readings.

Advantages.—Some of the special advantages of the new instrument are: the use of photocells eliminates the personal error in observations; the activation of the two photocells by lights from a single source avoids the errors of instability due to intensity fluctuations in the light source and the measurement through a sensitive and objective method of photometry by physical means, in the form of a variable light diaphragm and within a well-defined region of the spectrum gives greater precision to the measurements.

Applications

The apparatus can be put to a variety of purposes:

(1) Determination of concentrations of substances following the procedure described for phosphorus in the preceding pages. For other organic and inorganic estimations that can be done with the apparatus the methods given by Yoe[4] are applicable with the necessary modifications.

(2) Chemical investigations of colloids, *viz.*, studying the variation in turbidity of a colloidal solution under varying conditions such as temperature, etc.

(3) Certain enzymic studies; the apparatus has been specially useful in these laboratories for the study of *Amylase* and *Lipase* by the method of Hans Kleinman.[4] The former depends upon a homogeneous and stable colloidal glycogen solution acted upon by *Amylase* and the undigested glycogen estimated; the latter depends in splitting a homogeneous and stable emulsion of triolein by *Lipase*, the course of digestion being followed by comparison of the digested and undigested triolein solutions. The results of these studies will form a separate communication.

Summary

A new type of photoelectric nephelometer is described. The essential principle is the measurement of the intensity of scattered light coming from an illuminated column of turbid medium by a comparison with the light scattered from an invariable standard of turbidity (frosted glass) in a narrowly defined region of the spectrum with the aid of a quantitatively variable light diminution. Photoelectric cells are used to indicate equivalence of light.

The use of two photocells activated by light from a single source apart from eliminating the personal error in observations avoids the errors of instability due to intensity fluctuations of the light source. The measurement through a sensitive and objective method of photometry by physical means (in the form of a variable light diaphragm) and the use of light filters for measurements in narrowly defined regions of the spectrum give greater precision.

The accuracy of the apparatus is $\pm 2 \cdot 4$ per cent.

The several applications of the apparatus are described.

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THE DIAMAGNETIC SUSCEPTIBILITIES OF MERCURY IN VARIOUS STATES OF COMBINATION

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Received October 9, 1938

In three previous papers published from this laboratory the susceptibility constants for rubidium,[1] bismuth[2] and tin[3] have been calculated from their compounds. Further, in a note published in *Current Science*, the specific and atomic diamagnetic susceptibilities of mercury obtained from Kahlbaum's extra pure mercuric compounds are given. It has been shown that the values obtained from these compounds are almost the same as those obtained by E. Vogt,[4] Bates and Tai[5] and are slightly lower than those of Honda,[6] Owen,[7] and Davis and Keeping.[8] The higher atomic susceptibility obtained by Shur[9] in the vapour state and its close resemblance with the theoretically calculated value by Slater's method has been explained on the existence of mercury in the monoatomic state in vapour. The lower diamagnetic values of mercury in the liquid state have been attributed to the poly-atomic molecule of mercury on the assumption that the free electrons in the outer orbit of mercury may be interchanging between the component atoms to form an aggregate of poly-atomic molecule. In the present communication the diamagnetic susceptibilities of mercury in various states of linkages have been critically examined.

The small size of the ions and their double charge impart to the element the facility to pass into the covalent state and to form the covalent compounds with a variety of elements such as halogens, oxygen, nitrogen, and carbon. Mercury halides unlike the salts of alkaline earths are more volatile and more soluble in organic solvents. Their conductivities in the fused state are very small. No sharp distinction can be drawn between covalence and electro-valence as a substance like hydrochloric acid behaves as a covalent compound as a pure liquid and as an electrovalent one in solution. It is however definitely understood that the two types of valency do exist and can be distinguished from each other. There are also various intermediate types of linkages between strongly electrovalent rock salt and strongly covalent methane as follows :

(1) KCl, (2) HCl, (3) $HgCl_2$, (4) HgC_2N_2, (5) H_2O, (6) CH_4. Thus mercuric chloride is partly electrovalent and partly covalent as follows :

$$Cl - Hg - Cl \rightleftarrows Cl^- + Hg^{++} + Cl^-.$$

The diamagnetic constants for divalent mercury obtained by various workers are not the same. Meyer,[10] Pascal,[11] Wilsdon[12] and Kido[13] are notable amongst them. Their values vary from 31·2 to 46 while Pauling,[14] Slater[15] and Angus[16] get the theoretical values 55, 47·77 and 47·57 respectively.

(The values refer to $-\chi \cdot 10^6$).

Besides this, mercury forms double salts. It cannot always be assumed that a double salt really contains a complex molecule. There is a possibility of a crystalline aggregate formation of simple salt molecules. Mercury has a valency group of four electrons or a pair of covalent links. In presence of other salts, it can co-ordinate with one or two negative atoms such as chlorine, bromine and iodine. Thus the double salts can be represented as $KIHgI_2$ or $K(HgI_3)$ and $2KI\ HgI_2$ or $K_2(HgI_4)$. It has been referred to by Bhatnagar and Mathur in their book[17] that mercury, its halides, cyanide, and the double chlorides with potassium are all diamagnetic, but potassium iodomercurate on the other hand is paramagnetic. The question arises as to why it should be so. To understand more fully this behaviour, the magnetic properties of some double salts are also examined.

Further, mercury forms complex salts of uncertain structure particularly when these salts are dissolved in some organic solvents and the inferences drawn in literature from this behaviour are both ambiguous and vague. Considering the uncertainties of the work so far accomplished and the fact that many important conclusions may be derived from it, it was felt desirable to investigate mercury in various states of combination with the help of more sensitive and accurate instruments paying due regard to the purity of the materials employed.

Experimental

The apparatus employed for the determination of magnetic susceptibilities of solids was the magnetic interference balance devised by Bhatnagar and Mathur,[18] and manufactured by Messrs. Adam Hilger, Ltd., London. The sensitivity of this apparatus can be judged from the fact that a deflection of the tube of the order of 1/500 cm. corresponds to 600 divisions on the drum of the interferometer, and the accuracy of observation can easily be said to be one in one thousand. The values of χ_M given in the following tables have been calculated according to the formula :

$$\chi M = \chi_a M_a + (\chi_w m_w - \chi_a m_a) \frac{r - r_1}{r_2 - r_1}$$

where

χ = the magnetic susceptibility of the unknown substance ;
M = the mass of the substance taken ;

χ_a = magnetic susceptibility of air ;
M_a = mass of the air which fills the same volume as the substance ;
χ_w = magnetic susceptibility of water ;
m_w = mass of water ;
m_a = mass of air which fills the same volume as occupied by water ;
r = deflection with the unknown substance ;
r_1 = deflection due to the tube and air ;
r_2 = deflection with water and tube.

The values of susceptibilities have been checked up in a suitably modified form of Gouy's balance.[19] According to this method the susceptibilities can be calculated by the equation :

$$\chi_{d2} = \frac{1}{md_2}\left[(\chi_{d_1} m_{d_1} - \chi_a \cdot m_{ad_1}) \frac{Wd_2}{Wd_1} + \chi_a \cdot m_{ad2}\right]$$

where the letters have the usual significance.

The specific susceptibilities in the dissolved state have been determined by the aid of a modified form of Decker's balance.[20] The susceptibilities can be calculated according to the equation :

$$\chi_L = \frac{\phi_L\left[\frac{\chi_w - \chi_a}{\phi_w - \phi_a}\right] + \left[\frac{\chi_a\phi_w - \phi_w\phi_a}{\phi_w - \phi_a}\right]}{d}$$

where

χ_L = mass susceptibility of the solution ;
χ_a = mass susceptibility of the air ;
χ_w = mass susceptibility of the water ;
ϕ_L = angle of torsion due to the solution ;
ϕ_a = angle of torsion due to the air.
ϕ_w = angle of torsion due to the water ;
d = density of the solution.

In the case of solution, susceptibility of the salt has been calculated with the help of the relation :

$$\chi_L = \chi_{salt} \cdot C_{salt} + \chi_{solvent}(1 - C_{salt})$$

where C_{salt} denotes the concentration of the salts in solution.

The purity of the substances employed was of a very high standard and no substance was used unless its purity was established. Kahlbaum and Merck's extra pure specimens were re-purified, and their physical constants determined. The exhaustive qualitative and quantitative analyses were undertaken in order to test their purity.

The results obtained are tabulated below:

TABLE I

Specific Susceptibilities of Inorganic Mercury Compounds and the Susceptibility Constants of Mercury derived from them

Substance	Sp. Sus. Gouy's Balance $-\chi \cdot 10^6$	Sp. Sus. Interference Balance $-\chi \cdot 10^6$	Sus. Constants $-\chi \cdot 10^6$		
			Mol. Sus. $-\chi \cdot 10^6$	Sus. for −ve radicals $-\chi \cdot 10^6$	Sus. Constants $-\chi \cdot 10^6$
$HgCl_2$	0·313	0·3177	86·3	40·2	46·1
$HgBr_2$	0·305	0·3032	109·2	61·2	48·0
HgO	0·243	0·2432	52·7	4·6	48·1

Theoretical Susceptibility Constants

$-\chi \cdot 10^6$

55·0 (Pauling)

47·78 (Slater)

47·57 (Angus)

Specific Susceptibilities by other Authors

$HgCl_2$	0·301	(Vardhachari)
	0·298	(Kido)
	0·19	(Meyer)
	0·24	(Wilsdon)
$HgBr_2$	0·3	(Meyer)
HgO	0·24	(Meyer)
	0·243	(Mathur and Nevgi)

TABLE II

Specific Susceptibilities of Organic Mercuric Compounds and the Susceptibility Constants of Mercury in them

Substance	Sp. Sus. Gouy's Balance $-\chi \cdot 10^6$	Sp. Sus. Interference Balance $-\chi \cdot 10^6$	Sus. Constants $-\chi \cdot 10^6$		
			Mol. Sus. $-\chi \cdot 10^6$	Sus. for −ve radicals $-\chi \cdot 10^6$	Sus. Constants $-\chi \cdot 10^6$
Mercury-di-phenyl $Hg(C_6H_5)_2$	..	0·3984	141·3	104·5	36·8
Mercury-di-benzyl $Hg(C_6H_5CH_2)_2$	..	0·4270	163·4	128·3	35·1
N-propyl mercuric iodide C_3H_7-Hg-I	0·342	0·3408	126·3	83·25	43·05
N-butyl mercuric iodide .. C_4H_9-Hg-I	0·36	0·3588	138·0	95·15	42·85

Susceptibility Constants Obtained by Pascal

Substance	Susceptibility Constants $-\chi \cdot 10^6$
$Hg(CH_3)_2$	46·0
$Hg(C_2H_5)_2$	40·8
$Hg(C_5H_{11})_2$	35·4
Limiting value	33·1

TABLE III

Specific Susceptibilities of Inorganic Mercurous Compounds and the Susceptibility Constants of Mercury from them

Substance	Sp. Sus. Gouy's Balance $-\chi \cdot 10^6$	Sp. Sus. Interference Balance $-\chi \cdot 10^6$	Sus. Constants		
			Mol. Sus. $-\chi \cdot 10^6$	Sus. for −ve radicals $-\chi \cdot 10^6$	Sus. Constants $-\chi \cdot 10^6$
Hg_2Cl_2	0·305	0·3039	$(71·73)_2$	$(20·1)_2$	$(51·6)_2$
Hg_2Br_2	0·297	0·2970	$(83·33)_2$	$(30·6)_2$	$(52·7)_2$
Hg_2I_2	0·299	0·2995	$(98·09)_2$	$(44·6)_2$	$(53·5)_2$

By Kido $(40)_2$

TABLE IV

Specific Susceptibilities of Mercury Double Salts

Substance	Sp. Sus. Gouy's Balance $-\chi \cdot 10^6$	Sp. Sus. Interference Balance $-\chi \cdot 10^6$	Mol. Susceptibility $-\chi M \cdot 10^6$	
			Observed	Calculated
$HgI_2 \cdot KI$	0·355	0·3542	219·8	67·2 (KI) 143·0 (HgI_2) 210·2
$NH_4I \cdot HgI_2 \cdot H_2O$ ..	0·373	0·3722	229·8	66 (NH_4I) 13 (H_2O) 143 (HgI_2) 222

TABLE V

Specific Susceptibilities of Mercury Salts in the Pyridine Solution on Decker's Modified Balance

Substance	Sp. Sus. in solution $-\chi \cdot 10^6$	Sp. Sus. in the solid state $-\chi \cdot 10^6$
$HgCl_2$	0·2337	0·313
$HgBr_2$	0·1674	0·305

Discussion of Results

Several interesting points emerge from a closer examination of the results tabulated above. The results can be tested in the following five groups :

1. Mercury in the inorganic mercuric compounds.
2. Mercury in the organic mercuric compounds.
3. Mercury in the inorganic mercurous compounds.
4. Mercury double salts.
5. Mercury salts in the dissolved state.

1. *Mercury inorganic compounds in the bivalent state.*—The specific susceptibilities for the mercuric compounds are slightly higher than those recorded by previous authors (see Table I). Naturally, the molecular susceptibilities calculated from them came out to be higher. While finding out the

susceptibility constants for mercury in the bivalent state, the question arises as to what values should be taken for the negative radicals. In order to bring this point into prominence, an attempt has been made to calculate the susceptibility constants from one of the compounds, namely mercuric bromide by subtracting the different values of bromine obtained by various authors as follows :

$HgBr_2$:— Mol. Sus. $-\chi \cdot 10^6$	Sus. Constants $-\chi \cdot 10^6$	Values of —ve radicals $-\chi \cdot 10^6$
109·2	44·2	32·5 (Br) Reichendar
	46·4	31·4 (Br) Farquharson
	39·8	34·7 (Br) Kido
	48·0	30·6 (Br) Pascal

It is obvious that the constants are not the same. It has therefore been found desirable to calculate them by substituting the atomic values of Pascal for the negative radicals as the compounds exist mostly in the covalent state. No better values other than those of Pascal are at present available for the compounds in the covalent state. Accordingly the susceptibility constant comes out to be 46 to 48. The values cannot be compared with those obtained by other authors for the simple reason that they have made no distinction between the two kinds of linkages. It is rather curious to note that the susceptibility constants from the inorganic compounds are different from those derived from organic compounds. It has already been shown in the introduction that the compounds such as mercuric chloride are partly covalent and partly electrovalent.

$$Cl - Hg - Cl \rightleftarrows Hg^{++} + Cl^- + Cl^-.$$

It is well known that in going from the strongly electrovalent compounds, such as rock salt, to the strongly covalent compounds, such as methane, the sizes of ions are deformed. The sizes of covalent compounds are generally small. Thus the difference in the susceptibility constants mentioned above can very well be explained on the above assumption. The theoretical susceptibility constants obtained by Pauling, Slater and Angus are 55, 47·78 and 47·57 respectively. The present values closely correspond with the values calculated according to Slater and Angus.

2. *Organic mercuric compounds* (Table II).—It has already been pointed out that the susceptibility constants of mercury in organic compounds are lower than those which are obtained from the inorganic ones. Further, the

susceptibility constants from mercury-di-phenyl and di-benzyl are different from those which are derived from N-butyl and N-propyl-mercuric iodides. The former compounds are really the true organic ones while the latter are partly organic and partly inorganic. The susceptibility constants therefore should be midway between the constants from inorganic and organic compounds. The present results are therefore in agreement with this assumption. Further, Pascal has shown that the atomic coefficient of magnetization is not a constant quantity but it decreases with the increase of the molecular weight of organic radicals with which mercury is combined, approaching a limit 33·1. Perhaps, this may be the cause of the different values observed. It is rather interesting to note that the susceptibility constants from true organic compounds closely correspond with those which are obtained for liquid mercury.

3. *Mercurous compounds* (Table III).—The mercurous compounds are all diamagnetic. From this and a number of other facts it follows that these compounds exist in polymerised form. The susceptibility constants are between $(51.6)_2$ and $(53.6)_2$ while Kido has found it to be $(40)_2$. As has been pointed out, one is not completely justified in comparing the present values with those of Kido due to the different values for negative radicals substituted by him. However, the difference between the susceptibility constants of mercury in the ic and ous state is in the same direction and remains nearly the same.

4. *Double salts of mercury* (Table IV).—Mercury in the mercuric state contains a pair of normal covalent links. In presence of other salts such as potassium iodide, it can co-ordinate with one or two negative atoms. The number of linkages is thus increased by one or two. These are called co-ordinate linkages. The formation of the double salts may well be represented by saying that mercury acquires the necessary electrons from the combining salts. The constitutive atoms of the combining salts supply the necessary number of electrons to mercury. The exchange takes place as a donor and an acceptor. If a double salt is considered to be an aggregate of simple salts and is without any complex formation, the susceptibility of the salt should be additive. But the values obtained presently for these double salts are rather higher than those calculated from the additivity law. According to Bhatnagar, Verma and Kapur,[21] the co-ordinate formation causes an increment in the diamagnetism of some molecular compounds. The present results are therefore in line with them. The anomalous behaviour of potassium-iodo-mercurate could not be traced.

5. *Mercury compounds in the dissolved state* (Table V).—All the mercury salts being covalent are soluble in organic solvents in which they form

complex compounds. One is therefore, not completely justified in calculating the susceptibility constants from them. The specific susceptibilities in pyridine are rather low when compared with those in solid state.

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1946 38—Printed at The Bangalore Press, Mysore Road, Bangalore City, by G. Srinivasa Rao, Superintendent, and Published by The Indian Academy of Sciences, Bangalore